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PROGRAM & ABSTRACTS

SYMPOSIUM ON

Nonbiological transport and transformation of pollutants on land and water:

Processes and critical data required for predictive description

May 11-13, 1976
National Bureau of Standards
Gaithersburg, Maryland

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> *"Science is built up with facts as a house is with stones. But a collection of facts is no more a science than a heap of stones is a house."*
>
> Jules Henri Poincare
> *La Science et l'Hypothese*, 1908

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Program, abstracts and extended abstracts of 21 papers presented at a symposium on nonbiological transport and transformation of pollutants on land and in water are documented. Most of the extended abstracts are detailed and contain figures and references to pertinent literature on the subject matter discussed at the symposium.

The subject matter reviewed deals with the physical and chemical behavior of pollutants, including pollutant photochemistry, adsorptive behavior of pollutants, hydrolysis, rates of pollutants, and mathematical models for documenting pollutant behavior in soils and water.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*
Adsorption; nonbiological transformation; nonbiological transport; pollutant photochemistry; pollutants; soil pollution; solar spectrum; water pollution

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program

Tuesday, May 11, 1976

POLLUTANT TRANSFORMATION PROCESSES IN LAND AND WATER: SESSION I

Morning

Chairman: Lewis H. Gevantman, NBS

9:30 **Welcoming Address:** E. Ambler, Acting Director, NBS

9:35 **Opening Remarks:** C. Gerber, Associate Assistant Administrator for R & D, EPA

9:45 **Environmental Physics and Chemistry of Aquatic Pollutants**

J. C. Morris, Harvard University

For those aquatic pollutants that are not readily oxidized or degraded biologically the ultimate fates are determined by their physical and chemical properties in the aqueous medium. Some physical properties of significance are volatility, aqueous solubility, and adsorptive tendency, for these determine the likelihood that a pollutant will translocate into the air or the sediments. The chemical transformations by which organic pollutants are removed are generally either hydrolytic or oxidative, so that the susceptibilities of pollutants to hydrolysis or oxidation are chemical properties of major interest. Oxidation, in particular, may be either direct reaction with O_2, catalyzed oxidation, photooxidation or photosensitized oxidation.

Little is known about the relative importance of the individual physical and chemical properties in regulating the fate of specific aquatic pollutants under environmental conditions. Although there have been some observations of environmental persistence or changes from which mechanisms of transformation may be partially inferred, data are seldom quantitative or sufficiently detailed to predict the ultimate sinks of biologically perdurent materials. Field observations that can be correlated with laboratory data now being accumulated are badly needed.

10:30 **Coffee Break**

11:00 Prediction of Activities of Electrolytes in Natural Waters

Robert Wood, University of Delaware

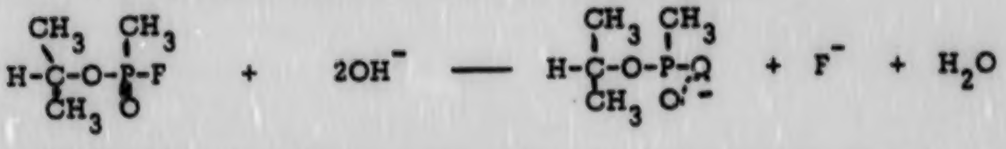
The development of various methods for predicting the properties of mixed electrolytes is reviewed, starting with the ionic strength principle and the mean salt methods of MacInnes, Harned, Lewis and Randall. In the last few years, equations have been developed which allow accurate predictions of the properties of mixtures of strong electrolytes. The accuracy of these equations in predicting the properties of seawater is demonstrated. The possibility of extending these calculations is discussed, together with the limitations of the method.

Possible ways of adjusting the newer equations for mixtures in which there is strong association is discussed. To refine and test these developments in the theory, it will be necessary to develop methods for making accurate measurements of all of the components of natural waters.

11:45 Reaction Rates of Electron Pair Donor Molecules with Pollutants in Water

John O. Edwards, Brown University

Many pollutants (including phosphorus insecticides and sulfur dioxide) react with electron pair donors (also termed nucleophiles, and in most instances these are reductants) to form new compounds less harmful to living systems and to the environment. For example, the anticholinesterases are converted to different chemical compounds which are not poisonous



$$H\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}O\text{-}\overset{CH_3}{\underset{O}{P}}\text{-}F + 2OH^- \longrightarrow H\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}O\text{-}\overset{CH_3}{\underset{O^-}{P}}\text{-}O + F^- + H_2O$$

although there remains an oxygen demand in the organo-phosphorus product. A general introduction into the chemistry of donors' interactions with substrates will be presented along with some aspects of reaction mechanism. The relative rates of donor reactions with several varieties or organic compounds, tetrahedral phosphorus species, compounds with cyano-groups, and metal complexes will be presented. Correlations of donor reactivity with basicity, electrode potential, polarizability, bonding nature, and the "alpha-effect" will be discussed on an empirical basis. Some generalizations that may be used for prediction of rates with new systems are now possible. The importance and value of hydrogen peroxide for treatment of polluted water will be detailed.

12:30 Lunch

Tuesday, May 11, 1976

POLLUTANT TRANSFORMATION PROCESSES IN LAND AND WATER: SESSION I

Afternoon

Chairman: Gunter Zweig, EPA

2:00 **Complexation, Precipitation, and Adsorption of Trace Metals in Water**

*J. J. Morgan** and Jasenka Vuceta, California Institute of Technology*

Metals introduced to natural waters are removed by precipitation, adsorption, and incorporation into biotic matter. Distributions of various metals between particulate and aqueous phases depend upon: pH, chemical and physical properties of different adsorbing surfaces, nature and abundance of complexing ligands in the solution phase, competition between metals for available ligands and surface sites, ionic strength, pε of the redox environment, and temperature. Predictive models must simultaneously consider all significant acid-base, solubility, complexation, redox, and adsorption processes. Adsorption models are briefly reviewed with respect to their treatment of chemical and electrostatic influences on metal ion distributions. Two models, the adsorption-hydrolysis, ion-solvent (AHIS) interaction model and the surface complex formation (SCF) model are considered in detail and applied to the description of complex natural water systems. The dominant role of pH in each of the models is illustrated; the influence of other solution composition variables on the distribution coefficient is examined. Three equilibrium multi-metal, multi-ligand system models are presented in which either AHIS or SCF descriptions of adsorption are employed. These systems models illustrate quantitatively the influences of pH, surface area, organic ligands, and preciptation processes on trace-metal distributions in water.

2:45 **Oxidation and Reduction of Pesticides in Soils and Sediments**

Jack R. Plimmer, U. S. Department of Agriculture

Several mechanicsms may be involved in the transformation of pesticides in soils and aquatic systems. Of these, transformation by microorganisms is predominant, but many purely chemical reactions may accompany biological pathways. The distinction between chemical and biological transformations in soils presents many experimental problems. Reactive intermediates may be generated in metabolic processes or arise by the action of free radicals in soil. Some chemical systems may be used as models to provide useful insights into the nature of the processes involved.

** *Speaker*

Reactions occurring in sediments depend on the availability of oxygen. Anaerobic processes will be favored as oxygen is depleted in sediments rich in organic nutrients. Measurement of redox potential may be a useful guide to potential reaction pathways.

3:30 Coffee Break

3:45 Kinetics of Hydrolysis and Oxidation of Organic Pollutants in the Aquatic Environment

*W. R. Mabey** and T. Mill, Stanford Research Institute*

Oxidation and free radical oxidation can be important degradation pathways for some organic pollutants in aquatic environments. Knowledge of the theoretical and experimental features of these reactions can be meaningfully applied to prediction of degradation rates and to design of experiments that are relevant to environmental conditions.

Three general hydrolysis mechanisms can be described. Depending on the compound, the hydrolysis kinetics may be acid and/or base catalyzed as well as being pH independent in a neutral reaction with water. The observed rate of hydrolysis may be due to any one or a combination of these mechanisms and will be determined by the pH and the temperature of the aquatic environment.

Oxidation of an organic molecule almost never involves a direct reaction with oxygen but usually involves an excited state or intermediate reactive radicals. One of the most common and best understood oxidation processes involves peroxy ($RO_2\cdot$) and alkoxy ($RO\cdot$) radical chains wherein three distinct types of radical processes are initiation, propagation, and termination. The kinetics of these processes can be quite complex and may include photochemical and various catalysis processes. While there is a vast body of data to evaluate these reactions, almost no detailed information is available on chemical oxidation reactions as they occur in aquatic environments.

** *Speaker*

4:30 **Chemical Degradation of Organic Pollutants in Soil**

V. H. Freed, Oregon State University

A number of reaction paths for organic pollutants in soil is theoretically possible. They may be categorized in the two major groups, namely biologically (including extracellular enzyme) mediated reactions, and "chemical" reactions. The focus of this presentation is on chemical or non-biological reactions exclusive of the oxidation-reduction reactions. These include such things as hydrolysis, complexation, and physical interactions. Much of the work on degradation of organic pollutants in soil has focused on pesticides. Since these compounds represent a number of classes of organic chemicals, they serve quite adequately as models for many of the organic pollutants. For many compounds, e.g. esters, amides, halogen substituted open-chain compounds, and others subject to nucleophilic attack, hydrolysis is much more rapid in soil than in aqueous solution. This has been attributed to catalytic influences of clay and organic matter, alkaline and alkaline earth ionic species, and overall pH. Other reactions leading to chemical degradation include complexation with some of the transition elements or sorption at specific loci on clay surfaces.

Because of the complexity of the soil system, precise mechanistic interpretation of rate data is often difficult. One must distinguish between biologically mediated reactions and the purely chemical ones. There are a few instances where this has been done, primarily with the organophosphates. Many compounds appear to follow a pseudo first-order kinetics, at least during some stages of degradation. In some compounds it has been found that a hyperbolic rate law more accurately describes the kinetics. However, rate studies have dealt with relatively low concentrations of the pollutant (in the order of 1 to 10 ppm) but in the few instances studied at higher concentration (100 to 1000 ppm) rate behaviors have been different.

5:30 Bus departs for Holiday Inn

Wednesday, May 12, 1976

POLLUTANT TRANSFORMATION PROCESSES IN LAND AND WATER: SESSION II

Morning

Chairman: Richard Zepp, EPA

9:30 The Photochemistry of Xenobiotics

Donald G. Crosby, University of California, Davis

For centuries, chemists have observed the effects of light on chemicals in the laboratory. However, it is only recently that investigation has extended to the sunlight-mediated transformations of foreign compounds--xenobiotics--under environmental conditions. Several characteristic reaction types now are recognized including oxidation, reduction, photonucleophilic displacements, elimination, and isomerisation. In addition to the chemical properties of the xenobiotic, the chemical nature of the surrounding microenvironment is an important determinant of its environmental fate. pH and photosensitizers in aquatic environments, interaction with air- and water-borne particles, and atmospheric composition all exert significant influence under laboratory conditions, but more emphasis on field investigations is needed.

10:30 Coffee Break

11:00 Solar Spectral Irradiance Reaching the Ground

Alex E. S. Green, University of Florida

Some of the basic elements of atmospheric radiative transfer which enter into the understanding of components of the solar spectral irradiance reaching the ground will be discussed. The simplest component, the directly transmitted component in most spectral regions can be calculated rather easily in terms of the incident solar flux, the total vertical thickness of each attenuating constituent and the zenith angle of the sun. The diffuse component of sunlight (skylight) which becomes very substantial at short wavelengths is difficult to calculate, and few groups are equipped to treat this component realistically. In a recent series of studies we have attempted to simplify the various theoretical approaches for ultraviolet radiation and cast their results into forms convenient for scientists concerned with biological consequences of this radiation. The influence of clouds greatly complicates matters and for the purposes of prediction or systematization requires data which are not currently recorded. However, we present approximate formulas based upon analyses and upon data which allow on the average for cloud effects. Our paper concentrates on light transmission and scattering problems in the ultraviolet and particularly the results of spectral irradiance values folded into a response curve of a biological system. The dose rate, daily dose, and annual dose reaching the ground varies with time of day and with the seasons in a fashion which may be represented by analytic functions of latitude, solar declination, and the parameters which characterize the atmospheric model.

11:45 Transmission of Sunlight in Natural Water Bodies

John E. Tyler, Scripps Institution of Oceanography

The basic concepts of radiometry are defined and illustrated and their application to the ocean for the purpose of determining the radiant energy available at various depths is illustrated. The use of radiant energy measurements for describing ocean types is discussed and the application of radiant energy data to the determination of the quantum efficiency of in-situ photosynthesis is discussed.

12:30 Lunch

Wednesday, May 12, 1976

POLLUTANT TRANSFORMATION PROCESSES IN LAND AND WATER: Session II

Afternoon

Chairman: Richard Carrigan, NSF

2:00 **Photosensitized Oxidation in Solution**

Christopher Foote, University of California, Los Angeles

Photosensitized oxidations proceed by a variety of mechanisms. In the Type I mechanism, there is a sensitizer-substrate interaction to give radicals which react further; in the Type II reaction there is energy transfer from sensitizer to oxygen to give singlet oxygen which reacts with many substrates. Methods of distinguishing these reactions and their complexities are discussed.

2:45 **Photolysis of Pesticides on Soil Surfaces**

Richard Hautala, University of Georgia

We have examined the photochemical decomposition of Sevin, Parathion, and 2,4-D on three different types of soil surfaces. The effects of anionic and cationic surfactant additives on the "rates" of photodecomposition have been studied. The moisture content of the soils was found to be a critical variable. Crude estimates of the quantum efficiency for photodecomposition indicate that photochemistry on soil surfaces is less efficient than the corresponding photochemistry in aqueous solution for all cases, but the variables described above exert strikingly different effects for each of the pesticides.

3:30 **Coffee Break**

4:00 **The Environmental Photodegradation of Selected Organometallic Complexes**

Haines B. Lockhart, Jr., Eastman Kodak

Synthetic chelating agents, such as EDTA, are used in our society. These chelating agents reach the aqueous environment via the discharge of wastes. Due to the concentrations of common metal ions in natural waters and the formation constants for the complexes formed between chelating agents and these metal ions, any study of the environmental fate of chelating agents must be, in fact, a study of these complexes.

In our studies, we have investigated the rate of photodegradation of buffered aqueous solutions of various X(N)-carboxyl-^{14}C-EDTA chelates in the presence of oxygen and simulated sunlight. In addition, photodegradation products of the most photosensitive common metal ion-EDTA chelate, Fe(III)-EDTA, have been identified and their generation studied over the pH range of natural waters.

The environmental implications of chelate photodegradation based on both our results and results recently published by others will be discussed.

4:45 **Predictive Modeling of the Behavior of Pollutants in the Aquatic Environment**

*R. R. Lassiter**, G. L. Baughman, J. L. Malanchuk, EPA*

A prototype model was constructed to classify the behavior and fate of substances with respect to specified environmental conditions, and to evaluate factors and processes important in their behavior and fate. Such models can be called evaluative models. The substance chosen for the prototype was the element mercury.

Forms of mercury represented are mercuric, elemental, and methyl mercury. These forms are assumed to exist in both water and sediment. The water is assumed to be moving over stationary sediments. Factors represented which potentially affect the fate of mercury are flow, water, and sediment depths, suspended particulates, and hydrogen ion concentration. Sorption and volatilization were found to be important processes affecting the fate of mercury as portrayed by the model. The need for measurement of parameters such as the partition coefficient for mercury forms bound to sediments is stressed.

5:30 **Reception**

6:30 **Buffet Dinner**

8:00 **Bus departs for Holiday Inn**

*** Speaker*

Thursday, May 13, 1976

POLLUTANT TRANSPORT PROCESSES IN LAND AND WATER

Morning

Chairman: David R. Lide, Jr., NBS

9:30 **Hydrologic Transport Processes for Pollutants in Water and on Sediments**

*Norman H. Crawford** and George Bailey, Hydrocomp, Inc.*

Hydrologic transport processes are described in both surface and groundwater. The variability of hydrologic transport from point to point in a field, and in different climatic zones is described. The development of computer based models for hydrologic transport is discussed, and the current and expected future applications of these models are outlined. The data requirements for analysis of hydrologic transport are discussed.

10:30 Coffee Break

11:00 **Vertical Movement and Distribution of Organics in Soils**

J. M. Davidson, University of Florida, Gainesville

The mobility and distribution of organic solutes in soils are dependent upon the physical and chemical characteristics of the soil, microbial degradation rate, and interactions between the solute and soil matrix. Chromatography theory has been used to describe solute movement and concentration distributions in soils. The adsorption-desorption of an organic solute in a soil-water system has been shown to follow a Freundlich equation. The velocity at which an adsorbed solute moves through a soil is independent of solute concentration for linear adsorption isotherms ($N = 1$) and concentration dependent for nonlinear adsorption isotherms ($1.0 < N < 1.0$). Adsorbed solutes have greater velocities at high solute concentrations ($C > 1.0\ \mu g/cm^3$) when N is less than 1.0. The concentration distribution of an adsorption isotherm is nonlinear ($N < 1.0$). The microbial degradation rate and solute velocity determine the depth to which an adsorbed solute front or pulse will move.

*** Speaker*

11:45 **Adsorption and Transport of Pollutants on Suspended Particles**

*B. T. Hargrave and K. Kranck**, Bedford Institute of Oceanography*

Many pollutants entering water, particularly those of low solubility, become associated with natural suspended material. Particle size and concentration determine the surface area available for adsorption and flocculation into units determined by inorganic grain size. Prediction of transport and dispersal of many aquatic pollutants is thus equivalent to prediction of the dynamics of fine-grained suspended material.

12:30 Lunch

** *Speaker*

Thursday, May 13, 1976

POLLUTANT TRANSPORT PROCESSES IN LAND AND WATER

Afternoon

Chairman: Ralph Franklin, ERDA

2:00 Environmental Transport Modeling of Pollutants in Water and Soil

*M. R. Patterson**, C. L. Begovich, D. R. Jackson, Oak Ridge National Laboratory*

A suite of models is discussed which can be applied to calculation of first order effects in transport of several types of pollutants in water and soil. The materials considered include solids in the form of particulates and soluble forms of the heavy metals. The time scale that is currently being emphasized is discussed, along with the physical size of the area covered by these calculations. The role of the hydrologic cycle is introduced along with the importance of bulk flow and particulate transport as suspended sediment. The build-up of lead, cadmium, zinc, and copper in the soil near a lead smelter over a six-year period is presented.

2:45 Prediction of Solubilization of Hydrophobic Organic Compounds in Water

Albert J. Leo, Pomona College

The mechanisms by which organic chemicals are dispersed into the environment as pollutants need a great deal of further study. In all environmental subsystems - land, atmosphere, inland waterways, or oceans - water appears to be a major carrier so a pollutant's water solubility and the manner in which it partitions between water and some lipid phase are important parameters to consider when constructing model systems and establishing quantitative relationships.

The partition coefficient P may have greater significance in these studies than water solubility per se. For organic liquids, the solution process can be considered as one of "self-partitioning."

Normally, most organic solids do not become pollutants until they become dissolved; once this has occurred, they are rarely removed from solution by recrystallisation but their availability and mobility may be altered by adsorption to a surface or by solution in an immiscible phase. These latter occurrences can often be modeled by use of the compound's partition coefficient between octanol/water.

The theoretical basis for the partitioning process is discussed and methods by which the log $P_{(oct)}$ can be predicted from molecular structures are given.

3:30 Coffee Break

4:00 Prediction of Volatilization Rate of Pollutants in Aqueous Systems

*Donald Mackay** and Yoram Cohen, University of Toronto*

In predicting the rate of volatilization of pollutants from aqueous environments the Whitman two film resistance approach is used, yielding a mass flux equation in which the three major parameters are the Henry's Law constant and the gas and liquid phase mass transfer coefficients. These three parameters are discussed in terms of the availability of data representation of environmental conditions, methods of obtaining such data experimentally or theoretically with emphasis on areas of inadequacy. Finally, some complications introduced by surface organic microlayers and the presence of interfering dissolved or particulate materials are outlined. It is concluded that the major areas of uncertainty are the value of the liquid phase mass transfer coefficient and the effects of other dissolved materials in modifying the Henry's Law constant of an evaporating pollutant.

4:45 Patterns of Deposition of Radionuclides in Sediments

*David N. Edgington**, Argonne National Laboratory, and*
John A. Robbins, The University of Michigan

Concentration profiles of ^{137}Cs, ^{210}Pb, and ^{239,240}Pu have been measured in sediment cores taken mainly from the southern end of Lake Michigan. Their measurement provides an accurate method for determining the rate of accumulation of sediments. The results indicate that the rate of accumulation of sediments in the lake is highly variable. They also indicate that there is a general redistribution of radioactivity in surface sediments from areas where there has been no significant deposition during the last 7000 years to areas where there is considerable sedimentation. Mechanisms such as these will be important in terms of understanding the effects and long-term fate of radionuclides (and other heavy metals) discharged into the lake. The differences in the shapes of the various profiles can be explained in terms of a constant (^{210}Pb) or a variable (^{137}Cs, ^{239,240}Pu) flux to the air-water interface with time, sedimentation rate, homogenous mixing due to physical or biological processes, and massive erosion or deposition due to storm activity.

EXTENDED ABSTRACTS

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HYDROLOGIC TRANSPORT PROCESSES FOR POLLUTANTS IN WATER AND ON SEDIMENTS

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A pollutant is any compound or substance that is undesirable where it is found. Transport processes often create a pollutant simply by moving a compound to a different environment. Nutrients are needed in the root zone in agricultural lands but are pollutants if they are moved into rivers or ground water aquifers.

Hydrologic transport is the movement of compounds in or by water. It may take place along any surface or subsurface path in the hydrologic cycle (Figure 1). The transport processes that are of interest in environmental studies of non-point pollution are:

(i) the movement of compounds in solution in runoff over the land surface, and the percolation of compounds in solution to ground water aquifers
(ii) the adsorption of compounds on soil particles, followed by the erosion and movement of the soil as sediment
(iii) the erosion of particles of compounds.

These processes are represented in the ARM Model[1] (Figure 2), developed for the Environmental Protection Agency to study the movement of pesticides and nutrients in agricultural lands.

Non-point pollution is very closely related to the hydrologic transport processes. Transport processes in nature are extraordinarily variable in time and space. Figure 3 shows the occurrence of overland flow in time for a watershed near Watkinsville, Georgia, in 1973. If overland flow carries sediment to a stream channel how does it move through the channel system? The transport of particles by streamflow is highly selective, and deposition and scour of particles takes place. Figure 4 shows the delivery of sediment particles to a channel system and the transport past a downstream gage. As point sources of pollution are more carefully regulated, diffuse or non-point pollution has become more important in meeting national water quality goals.

To develop public policies for the control of non-point pollution, a method must be available to predict the results of alternate policies. Its accuracy must be sufficient to correctly identify the best policies. Non-point pollution originates on the land surface, and policies to control land surface activities have important economic consequences.

How can alternate public policies be evaluated? How can changes in the hydrologic transport processes be predicted for alternate land uses or land surface activities? The possibilities are:

(i) field experiments on watersheds where policies are tested and the results are measured
(ii) computer based experiments with mathematical models of watersheds, on which policies can be tested and results obtained.

Field experiments are without question the best method to investigate a policy alternative for a given watershed. They give straight forward results that are understood by non-specialists. The use of chemical fertilizers is increased when farmers are supplied with samples for small plots in their own fields. Mathematical models must mimic complex transport processes and deal with esoteric topics like parameter estimation, calibration and verification.

The disadvantages of field experiments are the cost and the time needed to produce results. To investigate policies for one non-point pollutant at one location might require five years and 100,000 dollars. Sampling all climates and soils for the major pollutants would require thousands of watersheds throughout the United States and many years of experimentation.

Mathematical models can generate in minutes all of the data that could be measured in a five year field experiment. A model can, if suitable parameters are estimated, generate results for ungaged watersheds. The advantages of mathematical models are not obtained without cost, and models can easily be misused. A summary of requirements for successful model development and application is:

(i) the physical processes that control watershed response must be identified, and represented in the model by algorithms
(ii) the model must operate from input data that exists, or from data that can be obtained with reasonable effort
(iii) the model must calibrate to reproduce historic watershed response, and must be verified by forecasting or predicting other periods of watershed response
(iv) data series for hydrologic transport processes that are generated by models should be continuous over sufficient time periods to allow statistical analysis for means and extremes.

Success in modeling is relative. If the expected accuracy of model output can be established, and if this accuracy is sufficient to select a correct public policy alternative, then the model is a success. Establishing the expected accuracy of model output requires care, and strict attention to algorithm design, input data, calibration, and verification.

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[1] Modeling Pesticides and Nutrients on Agricultural Lands, Research Grant R 803116-01-0, Office of Research and Development, Environmental Protection Agency.

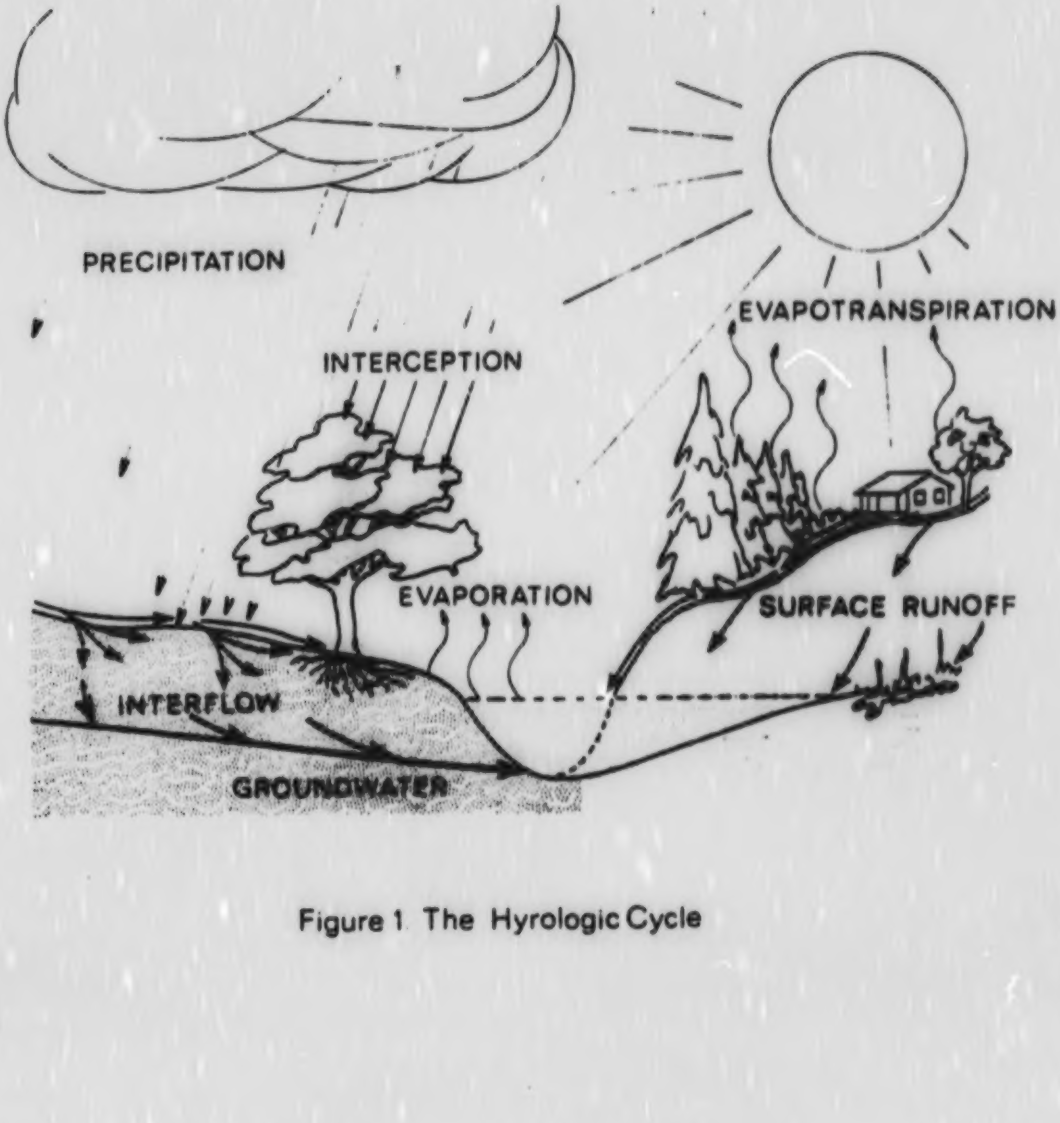
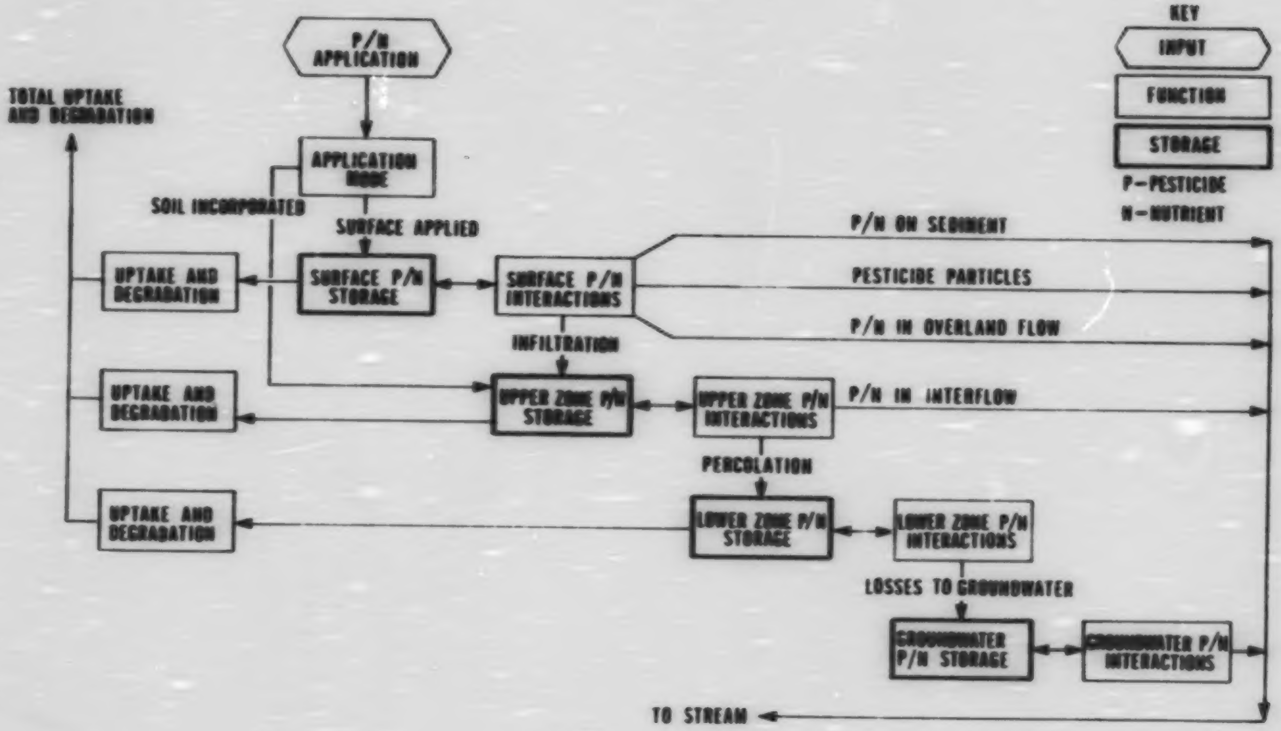

PRECIPITATION
INTERCEPTION
EVAPOTRANSPIRATION
EVAPORATION
SURFACE RUNOFF
INTERFLOW
GROUNDWATER

Figure 1 The Hyrologic Cycle

Figure 2
Pesticide and Nutrient movement in the ARM model


KEY
INPUT
FUNCTION
STORAGE
P—PESTICIDE
N—NUTRIENT
P/N APPLICATION
APPLICATION MODE
SOIL INCORPORATED
SURFACE APPLIED
TOTAL UPTAKE AND DEGRADATION
UPTAKE AND DEGRADATION
SURFACE P/N STORAGE
SURFACE P/N INTERACTIONS
P/N ON SEDIMENT
PESTICIDE PARTICLES
P/N IN OVERLAND FLOW
INFILTRATION
UPPER ZONE P/N STORAGE
UPPER ZONE P/N INTERACTIONS
P/N IN INTERFLOW
PERCOLATION
LOWER ZONE P/N STORAGE
LOWER ZONE P/N INTERACTIONS
LOSSES TO GROUNDWATER
GROUNDWATER P/N STORAGE
GROUNDWATER P/N INTERACTIONS
TO STREAM

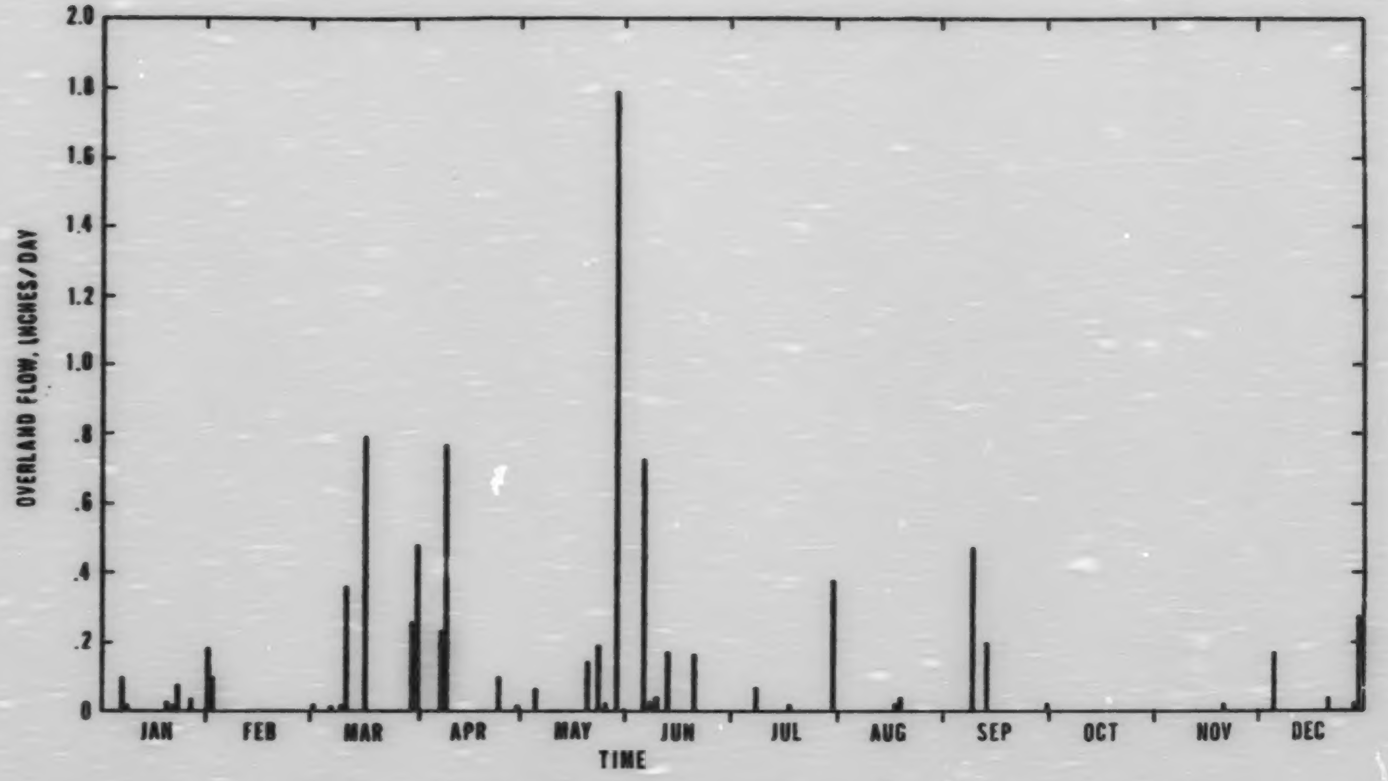


Figure 3. Overland flow in P1 watershed, Watkinsville, Georgia 1973

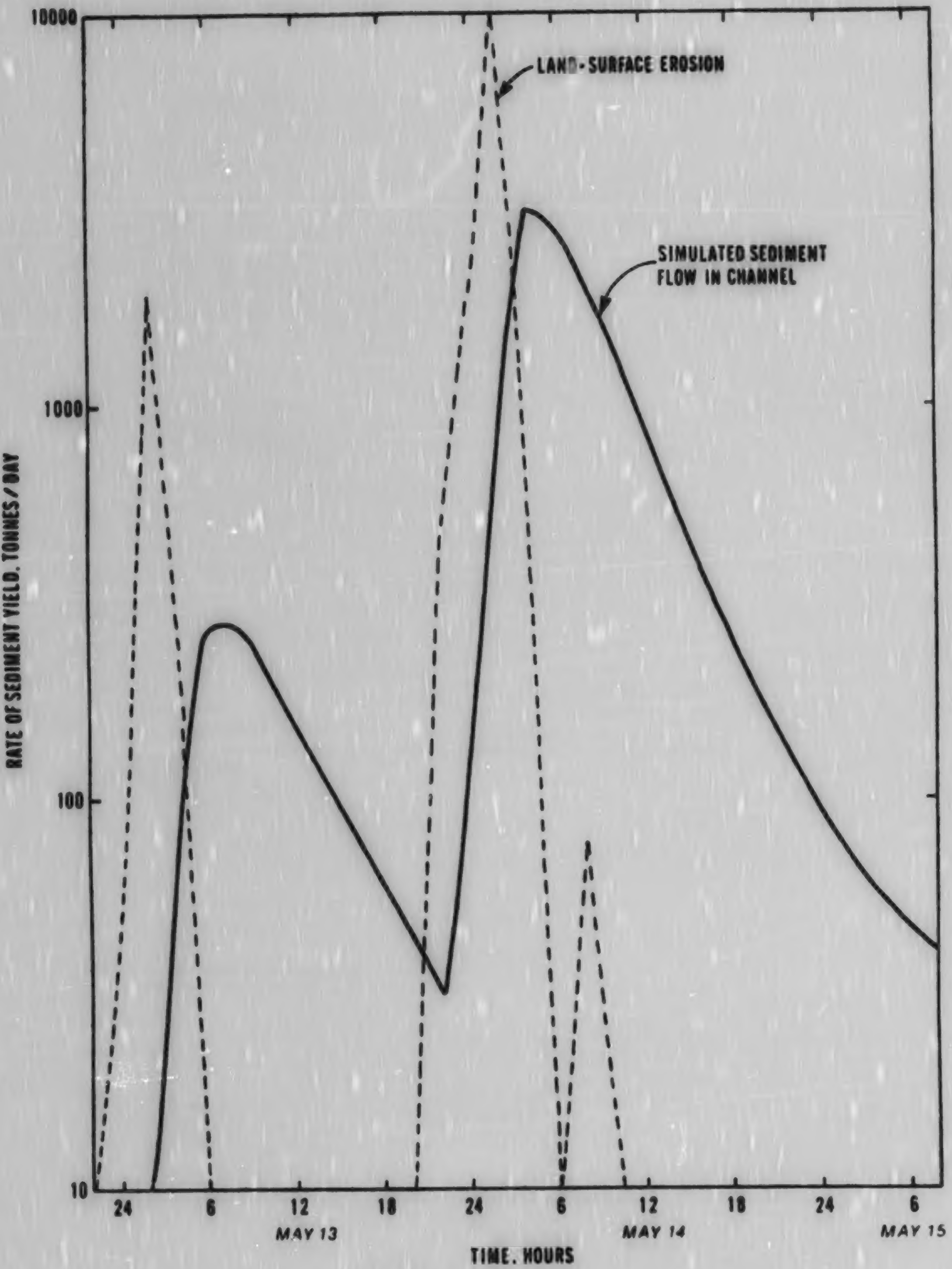


Figure 4. Sediment transport in Four Mile Creek, Iowa–May 1970

THE PHOTOCHEMISTRY OF XENOBIOTICS

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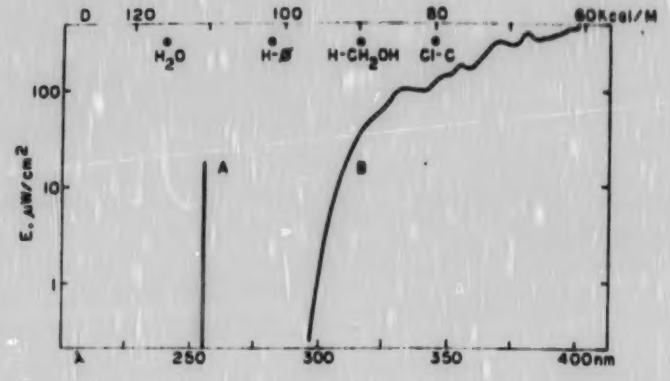
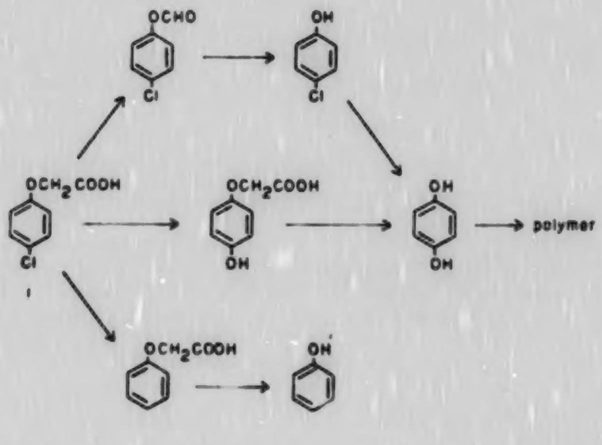
For centuries, chemists have observed the effect of light on chemicals in the laboratory. However, it is only in recent years that investigation has extended to the action of sunlight on the foreign chemicals dispersed in the environment--the "xenobiotics." While not so energetic as most common laboratory light sources, the ultraviolet portion of sunlight (Scheme A) nevertheless provides sufficient energy to bring about several important types of photochemical transformations (1).



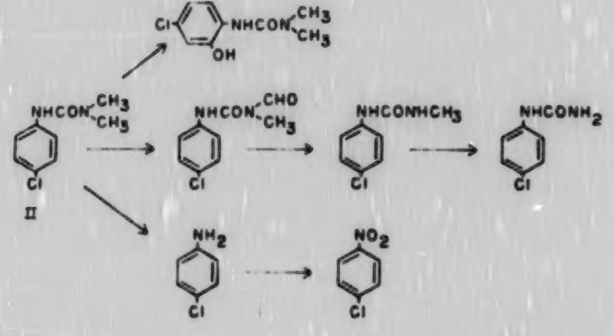
Scheme A

Oxidation, reduction, and photonucleophilic displacements are most often represented, as demonstrated by the growth regulator p-chlorophenoxyacetic acid (I, Scheme B). A free-radical oxidation removes the side-chain, reductive dichlorination replaces the ring Cl with H, and hydroxide ion (from water) replaces the Cl with OH (2).



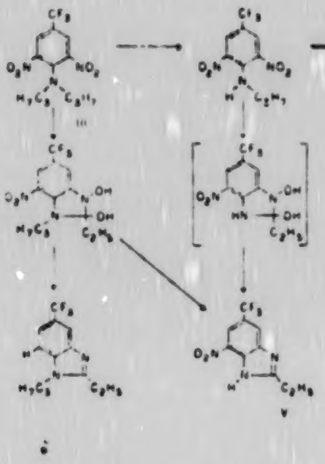
Scheme B

The herbicide monuron (II, Scheme C) provides further examples of oxidation. The N-methyl groups are oxidized to formyls subsequently removed by hydrolysis or loss of CO. Alternatively, the aromatic ring is hydroxylated ortho to the urea side-chain. Further, the p-chloroaniline resulting from hydrolysis is oxidized to the corresponding azobenzene or even to p-chloronitrobenzene (3).

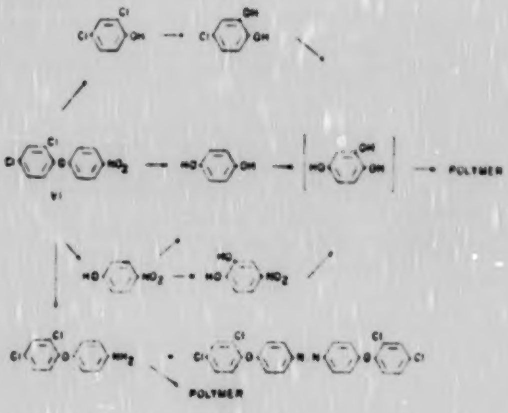

NHCON(CH3)CH3
Cl
OH
NHCON(CHO)CH3
NHCONHCH3
NHCONH2
II
NH2
NO2

Scheme C

The herbicide trifluralin (III, Scheme D) likewise is oxidatively dealkylated but also undergoes reduction of nitro group to the amine IV (4). A similar reduction occurs in nitrofen (VI, Scheme E), although the predominant reaction is photonucleophilic displacement of p-nitrophenate and nitro groups by hydroxide to provide various phenols (5).

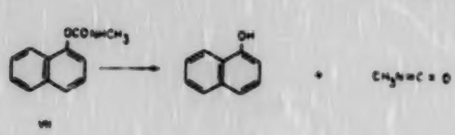

CF3
O2N
NO2
III
IV
V

Scheme D


VI
POLYMER
POLYMER

Scheme E

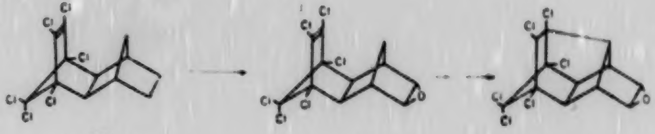
Other common sunlight-energized reactions include elimination (methyl isocyanate from 1-naphthyl N-methylcarbamate, carbaryl, Scheme F VII) and isomerization (dieldrin to the half-cage isomer X, Scheme G) (6,7).


OCONHCH3
OH
VII
CH3N=C=O

Scheme F

In the natural environment, xenobiotics generally are in contact with a large molar excess of reagents--for example, the hydroxide ion concentration in sea water is about 10^{-6}M while that of DDT typically is on the order of 10^{-11}M. Consequently, the chemical nature of the immediate microenvironment in which the xenobiotic occurs is an extremely important determinant of the compound's eventual fate. However, that nature frequently is widely variable and often unknown, and so our ability to simulate outdoor reaction conditions in the laboratory is quite limited (8,9).

For example, the relative proportions of trifluralin photoproducts depends upon pH; the benzimidazole V is not observed at pH 5.5 but constitutes 80% of the mixture of pH 11.0 (10). However, the pH of natural waters can range from 3 to 10, and the concentrations of other natural nucleophiles such as ammonia also vary widely. Apparently, external oxidants other than oxygen also can be generated in water, so photoxidation is not always dependent upon absorption of ultraviolet light by the xenobiotic. The olefinic insecticide aldrin (VIII) can be converted in water to its epoxide, dieldrin (IX) (11), although neither substance absorbs sunlight (Scheme G).



VIII IX X

Scheme G

In the vapor phase, the types of transformations open to xenobiotic are much more restricted. For example, in the laboratory trifluralin undergoes oxidation and cyclization but not reduction (12), and nitrofen is inert. However, the natural atmosphere also contains water, organic-rich particulate matter, photochemical oxidants, etc. Inorganic surfaces such as silica must exert a strong influence, for example allowing the conversion of nonabsorbing 1,3-dichloropropene to the corresponding epoxide and its subsequent rearrangement product 3-chloropropionyl chloride (13).

Considering the steadily increasing volume of "foreign chemicals" being delivered to the environment and the magnitude of the forces which act on them, our knowledge of the photochemistry of xenobiotics is only rudimentary. Among other things, we need information on the types of compounds entering our air and water and the chemistry of their microenvironments; better ability to simulate, sample, and analyze the environmental compartments; and realistic evaluation of the environmental toxicology of the xenobiotics in relation to their natural fate.

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VERTICAL MOVEMENT AND DISTRIBUTION OF ORGANICS IN SOILS

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The movement of organic solutes through soils occurs as a result of molecular diffusion and mass transport in the soil-water phase. Molecular diffusion is a relatively slow process in comparison to mass transport; therefore, it will not be considered a major transport process in this manuscript. Organic solute movement by mass transport is dependent upon the physical and chemical characteristics of the soil and interactions between the solute and soil matrix. An understanding of how these processes influence the transport of various organic chemicals is required in order to predict and manage the behavior of toxic organic solutes in natural soil-water systems.

Several mathematical models have been proposed to describe the movement and distribution of solutes in porous media (1-5). These models are based on chromatography theory and vary in their conceptual description of the physical characteristics of the soil-water system and interactions between the solute and soil matrix. Because of the general acceptance of chromatography theory and its applicability to a soil-water system, this approach will be used in the following discussion to describe the vertical movement and distribution of organic solutes in soils. Experimental verification of the above models for steady state and transient soil-water conditions is available (5-9).

The movement of organic solutes through soils will be assumed, for discussion purposes, to be described by the following partial differential equation.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \frac{\rho}{\theta}\frac{\partial S}{\partial t} - kC \qquad [1]$$

where C is the organic solute concentration ($\mu g/cm^3$), t is time (hr), D is dispersion coefficient (cm^2/hr), z is vertical depth (cm), v is average pore-water velocity (cm/hr) given by dividing Darcy's flux by volumetric soil-water content, ρ is soil bulk density (g/cm^3), θ is volumetric soil-water content (cm^3/cm^3), S is the adsorbed organic solute concentration ($\mu g/g$), and k is rate coefficient for microbial degradation (hr^{-1}). The first two terms on the right hand side of equation [1] describe solute transport, while the third and fourth terms describe the adsorption-desorption process and the irreversible loss of an organic solute from the system by microbial degradation, respectively.

The adsorption-desorption of most organic chemicals in a soil-water system has been shown to follow a Freundlich equation (10,11). The relationship assumes adsorption equilibrium exists at all times. Using this relationship to describe adsorption-desorption and the procedure outlined in Hashimoto et al. (1), equation [1] becomes:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - kC \qquad [2]$$

where, the retardation term R is:

$$R = 1 + \frac{\rho}{\theta} NKC^{N-1} \qquad [3]$$

and K and N are the distribution coefficient (1,10,11) and exponent from the Freundlich equation. The adsorption-desorption of some organic solutes is not instantaneous, but a kinetic process requiring several hours for equilibrium. Kinetic adsorption-desorption equations have also been used (2,4,6) in equation [2].

The simultaneous movement of water and organic solutes through natural field soils is generally a transient process. The direction and rate at which the two phases move depend upon various physical, chemical, and biological processes. The transient nature of the problem, however, makes it difficult to evaluate specific processes. Therefore, in order to discuss the basic mechanisms influencing the movement and distribution of organic solutes in soils, steady state soil-water conditions will be considered here.

The movement and distribution of organic solutes in soils will be discussed using equations [2] and [3]. The average pore-water velocity, v, in equation [2]is also the velocity at which a nonreactive solute front or pulse moves through a soil (e.g. chloride or tritium). Dividing both sides of equation [2] by R gives a reduced velocity, v/R, which is the velocity of an adsorbed solute front or pulse in a soil. This velocity depends upon the adsorption-desorption characteristics of the organic solute and soil (K, N). The sink term (kC) for microbial degradation does not influence the velocity of an organic solute. The magnitude of k and and v/R determine the maximum soil depth to which an organic solute will move and the concentration distribution of the solute in the soil (12,13).

Figure 1 contains four general adsorption isotherms that have been observed for various organic chemicals and adsorbents (14). Isotherms A, B, and C in Figure 1 are described by the Freundlich equation (1,10, 11) and that in Figure 1D by the Langmuir equation (14). Using the adsorption isotherms in Figure 1 and equation [2] and [3], it is possible to describe the relative mobility of different organic solute concentrations in a soil.

The velocity at which an organic solute front or pulse moves through a soil is independent of the solute concentration when $N = 1.0$ in equation (3) (Figure 1A). Thus, the mobility of the organic solute depends upon the soil-water flow rate and distribution coefficient, K. The assumption of a linear adsorption isotherm is frequently made regarding organic chemicals at low concentrations (4,7,11). If the organic solute was introduced into the soil as a pulse, the shape of the pulse in the soil (concentration distribution with soil depth) would be reasonably symetrical. The distribution of the organic solute in the soil is influenced by the change in soil-water flow direction with time (e.g., evaporation from the soil surface) and dispersion coefficient, D, (mechanical mixing owing to pore size distribution). When water evaporates from the soil surface, a net upward movement of the organic solute occurs. This results in a spreading of the solute concentration distribution and reduction in maximum solute concentration.

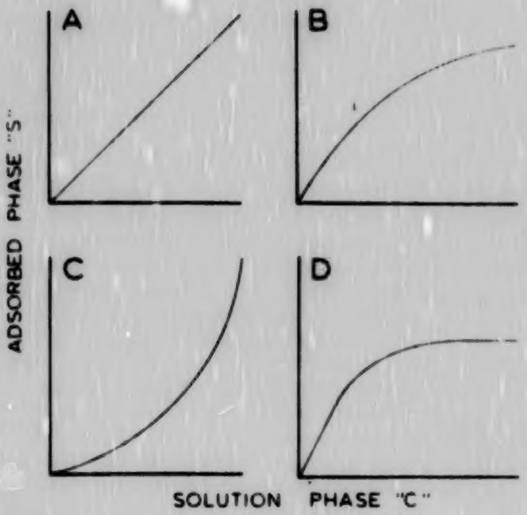

Figure 1. Typical adsorption isotherms for organic solutes in soil-water systems.

If the adsorption isotherm is nonlinear (Figures 1B and 1C), the average velocity, v/R, of the organic solute will depend upon the solute concentration (equation 3) as well as K. Several investigators have observed a deeper penetration of organic solutes with an increase in the chemical concentration (15-17). Organic solute mobility is greater in systems where $N < 1.0$ (Figure 1B) than where $N > 1.0$ (Figure 1C). Note that the retardation term is the same when $C = 1.0$ $\mu g/cm^3$ (equation 3). The importance of the adsorption isotherm shape is more pronounced at high than at low organic solute concentrations (<10 $\mu g/cm^3$). For example, if $\rho = 1.5$ g/cm^3, $\theta = 0.35$ cm^3/cm^3, $K = 1.0$ cm^3/g and $N = 0.7$, the retardation terms for $C = 10$, and 1,000 $\mu g/cm^3$ using equation [3] are 2.50, and 1.38. For $N = 1.3$ and $C = 10$ and 1,000 $\mu g/cm3$, the retardation terms are 12.1 and 44.3, respectively. The retardation terms for $N = 1.3$ increase sharply with an increase in solute concentration (equation 3 and Figure 1C). The concentration distribution of a pulse of organic solute will spread over a greater soil depth when $N < 1.0$ than when it is equal to unity. The spread or "tailing" of the solute concentration distribution occurs behind the invading front of the pulse.

A summary of available data on adsorption of organic chemicals in soils and the Freundlich equation parameters that describe the isotherms are given in Hamaker and Thompson (11). There is a tendency for N = 1.0 to approximate many adsorption isotherms, but there are also many values significantly lower than unity. The value of N appears to vary between 0.7 and 1.0. Deviations from linearity are more obvious when large concentration ranges are considered. From the previous discussion, it would appear that if the widely used assumption of unity for N was not valid, considerable error would be introduced in calculating organic solute movement and concentration distributions.

The mobility of an organic solute in a soil with an adsorption isotherm described by the Langmuir equation (Figure 1D) is also concentration dependent. At solute concentrations high enough to saturate the adsorption sites, the organic solute mobility is equal to that of a nonadsorbed solute. At lower concentrations the results are similar to the case for N < 1.0 in the Freundlich equation.

If the adsorption process was kinetic, and the soil-water flow rate was great enough to prevent equilibrium adsorption, the solute concentration distribution in the soil would be spread over a greater soil distance than occurs for equilibrium adsorption (4,5,6). These types of processes have not been studied in detail for organic solutes and soils. Kinetic adsorption equations may also be nonlinear.

The significance of microbial degradation, kc, to organic solute mobility is in the depth to which the solute will move (12, 13). If degradation is rapid and the reduced velocity, v/R, is low, the maximum depth to which the organic solute will penetrate the soil profile is small. Organic solutes with large transport velocities move deeper into the soil profile than those with low velocities.

There appears to be no consistant procedure for grouping organic chemicals with regards to their mobility in soils. The adsorption-desorption characteristics for each chemical varies with the soil or adsorbent. The mobility and distribution of a chemical can only be estimated after the adsorption isotherm has been determined. Also, the transient nature of the soil water is important in increasing the soil profile length over which the organic solute is spread. Care should be exercised in making general statements about the mobility of organic solutes in soils in the absence of adsorption-desorption data.

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PATTERNS OF DEPOSITION OF RADIONUCLIDES IN SEDIMENTS*

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During the last twenty-five years, considerable attention has been given to the study of the distribution of natural and artificial radioactivity in the oceans. From these studies, it has been possible to develop a greater understanding of the physical, chemical and biological processes occurring in the oceans. These studies have centered around either the patterns of deposition of fallout from nuclear testing and the interaction with biotic or abiotic components in the water column (1), or the dispersal of radioactivity from the disposal of radioactive wastes into rivers such as the Columbia (2) or coastal waters such as the Irish Sea (3) or Bombay Harbor (4). These studies show that most of the radioactivity is either in the sediments or dissolved in the water; there is only an extremely small fraction in the biota (5). As a result of these studies, it is possible to predict in general terms the behavior not only of radionuclides, but also many other known or potential pollutants.

In contrast to the extensive data accumulated for the behavior of radionuclides in the oceans, comparatively few historical data are available for the Great Lakes. Recently, Wahlgren and Marshall have reported measurements of ^{239,240}Pu, ^{137}Cs, and ^{90}Sr in the water and biota of these lakes (6), and Edgington and Robbins have reported measurements of ^{239,240}Pu, ^{137}Cs, and ^{210}Pb in their sediments (7). These results show that while phytoplankton may play a significant role in scavenging plutonium and cesium from the water column, greater than 95% of the known inputs of these radionuclides (from nuclear testing) now reside in the sediments. Wahlgren and Nelson have also shown that the concentrations of plutonium and cesium in suspended matter from the water column are very comparable to those in the surficial sediments (6). Studies of the distribution of trace elements in sediment cores from the lakes have shown that the concentrations of many heavy elements are elevated in the upper few centimeters of the sediment column (8). More recently, Edgington and Robbins have demonstrated that the shape and magnitude of the lead profiles in sediment cores from southern Lake Michigan can be explained in terms of the history of atmospheric lead deposition into the lake from the Chicago-Milwaukee region (9).

Since many pollutants, such as lead, mercury and plutonium are strongly associated with suspended matter or sediment, it is clear that the deposition, resuspension and redistribution of sediments with time may be of primary importance in determining their eventual biological fate. The processes of sedimentation may alter the distribution of a pollutant in such a manner that high concentrations may be contained in local areas which could have adverse effects directly on man, or on the benthic and other components of the aquatic environment.

In this paper, we shall report on the measurement of concentration profiles of ^{137}Cs, ^{210}Pb and ^{239,240}Pu (to be referred to as ^{239}Pu for convenience) in sediment cores taken mainly from southern Lake Michigan. The stations are shown in Figure 1. Since the only significant inputs of these radionuclides have been from atmospheric fallout, it is assumed that the input flux over the lake has been constant and, therefore, variations in the flux at

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*Work performed under the auspices of the U.S. Energy Research and Development Administration.

the sediment-water interface are indicative of redistribution of the sediment. The profiles are interpreted in terms of a simple model described by Robbins and Edgington (10), which permits the calculation of sediment rate, a mixing depth which is indicative of the degree of surficial disturbance due to biological or physical disturbances, and the total deposition per unit area. The results are shown in Table 1.

The patterns of post-glacial sedimentation in Lake Michigan as measured by seismic profiling (11) show that the deposition of post-glacial sediments is quite variable. However, the uppermost 1 or 2 centimeters of sediment consist of a highly liquid, reddish-brown flocculent material which contains high concentrations of radionuclides and trace elements, independent of the sedimentation rate or characteristics of the underlying material. Robbins has shown that the chemical composition of this floc is not significantly different than that of underlying fine-grained sediments (12). The relationship between sedimentation rates calculated from the ^{210}Pb or ^{137}Cs profiles, and from the thickness of the Waukegan member, the uppermost stratigraphic layer in southern Lake Michigan is shown in Figure 2. The apparent correlation suggests that the present rate of sedimentation in the lake is not significantly different from the average rate over the last 7000 years.

The cesium or plutonium deposition in the lake is compared with sedimentation rates in Figure 3a and b. Values of the sedimentation rate, mixing depth and the flux normalization factor f, defined as the ratio of the observed deposition in the sediments to that expected to be present if there was direct coupling between the input at the air-water interface and the sediment are given in Table 1. Values of the ratios of f indicate that the scavenging of cesium is very similar to that of plutonium, i.e., $f\text{Pu}/f\text{Cs} \approx 1$, while that of lead is quite different, the values of fPb/fCs being quite variable. However, it does appear that, in general, the higher values of fPb/fCs are found at stations well offshore. The similarity in the behavior of cesium and plutonium is surprising considering their very dissimilar chemical properties. Recent experiments by Alberts and Wahlgren (13) using techniques described by Gibbs (14) have shown that: (a) plutonium is primarily associated with reducible hydrous oxides; (b) cesium is associated with the clay minerals; and (c) lead is associated with organic matter. Since Shimp et al. have shown that hydrous oxides, like Fe_2O_3, are strongly correlated with the <2 μm clay fraction and the proportion of organic material increases with increasing distance offshore (8), the similar scavenging of plutonium and cesium, and the inshore-offshore differences in the scavenging of lead are as expected.

The isopleths shown in Figure 3a and b indicate that the total deposition of ^{239}Pu or ^{137}Cs in the sediments is very strongly correlated with the magnitude of the sedimentation rate and that the areal distribution of these nuclides in the sediments is, therefore, very non-uniform. The data indicate that there is considerable resuspension and transport of sediment from the western side of the lake, where there is a 1—2 cm thick layer of floc overlying glacial till or lacustrine clay, to the areas of high deposition, about 12 miles from the eastern shore, where both the rates of sedimentation and radioactivity deposition are highest. This pattern of deposition is interesting. Although the bottom topography indicates an almost continuous slope downward in a westerly direction to the maximum depth of 180 m, the maximum deposition of sediment occurs at a water depth of only 80 m. In addition, no sedimentation or deposition of radioactivity occurs at water depths of less than 50 m, even on the eastern side of the lake where several large rivers discharge. From this and the fact that Wahlgren and Nelson have shown that the residence time of plutonium and cesium in the water column is very short (15), it is concluded that radioactivity which may be released into the nearshore zones from nuclear power plants would be rapidly transported to the region of high sedimentation. In summary, any monitoring scheme for determining the long-term effects of releases from nuclear plants must take into account the sedimentological properties of the receiving body of water, i.e., the final point of deposition may be far removed from the site of release.

Evidence for transport and redeposition of sediments in Lake Michigan can also be deduced from a detailed examination of the profiles of radioactivity in the sediment column. Since the flux to the lake of ^{210}Pb, which is produced in the atmosphere from the decay of terrigenous ^{222}Rn, is constant with time, the ^{210}Pb concentration should decrease exponentially with depth if the sedimentation rate has been constant, and if there have been no physical and/or biological disturbances of the sediment after deposition. Such a profile, obtained from a core taken from a water depth of 300 m is shown in Figure 4. The line through the points was calculated from a simple exponential model (10). Numerous cores have shown similar profiles for ^{210}Pb. However, in others, the concentration of ^{210}Pb is constant over several centimeters at the top of the core. This is indicative of mixing due to physical processes and/or bioturbation in the lake. The data obtained from the analysis of several cores from Lake Huron show that the depth of mixing coincides with the detection of benthic organisms (12).

The two ^{210}Pb profiles shown in Figures 5 and 6 indicate even greater evidence of redistribution of the sediment after deposition. The profile shown in Figure 5 shows a break at 5 cm which is equivalent to 35 years or 1938. The decreased activity of ^{210}Pb below 5 cm would indicate a much lower sedimentation rate, or even erosion, at that time. On the other hand, the profiles shown in Figure 6, which are for two cores taken at the same station a year apart, are characterized by several breaks. Zones of constant activity correspond to an infinite sedimentation rate, and no elapsed time can be associated with such intervals. These could be due to massive redistributions of sediment or slumping. The zones of constant activity correspond to the dates of 1958, 1940 and 1915, respectively. Similar breaks corresponding to similar dates have been found in many cores from Lake Michigan and Lake Erie. As these dates correspond to the years of major storms in the Great Lakes, these results suggest that storm induced translocation and redeposition of sediments may occur in water over 70 m in depth.

The ^{137}Cs and ^{239}Pu profiles from some cores also indicate that considerable redeposition of sediment is occurring. Since the inputs of these two radionuclides to the lake has been extremely variable (the inputs are dependent upon the intensity of nuclear testing), the profiles in the sediments should reflect this time dependence. Such profiles are shown in Figures 7 and 8. The dashed lines were calculated using the mixing model described by Robbins and Edgington. The maxima in the concentrations of ^{137}Cs or ^{239}Pu correspond to the maximum fallout deposition in 1963, and the horizon of zero activity to 1951 or 1952. In contrast to the profiles shown in Figure 7, the intensity of the maximum in Figure 8 is depressed. This is probably due to the effect of surficial mixing. While the deposition of nuclear fallout in 1972 was more than an order of magnitude lower than in 1963, the concentration of ^{137}Cs or ^{239}Pu in the upper centimeter is less than a factor or two lower. As the estimated inputs of these radionuclides from the watershed are less than new direct inputs of atmospheric fallout (16), these high concentrations of cesium and plutonium can only arise from remobilization and redeposition of surface sediment in the lake.

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TABLE 1. Summary of measured and calculated parameters from the distribution of ^{210}Pb, ^{137}Cs and ^{239}Pu in Lake Michigan sediment cores.

Station	Sedimentation Rate		Mixing Depth (cm)	Flux Normalization Factor			Flux Ratios		
	(cm/yr)	(mg/cm^2/yr)		fPb	fCs	fPu	Pb/Cs	Pb/Pu	Cs/Pu
72-54	0.02	5.9	1.0	0.91	0.59	0.58	1.54	1.55	1.01
72-17	0.066	15.0	0	0.90	0.24	0.30	3.75	3.00	0.80
73-8	0.10	14.5	2.0	2.43	0.88	0.48	2.76	5.06	2.08
73-7	0.18	32.1	0	3.32	1.15	0.95	2.88	3.49	1.21
73-6	0.23	43.4	0	3.80	1.04	0.65	3.65	5.84	1.60
73-5	0.20	40.4	0	2.94	1.03	0.80	2.85	3.67	1.29
73-4	0.18	41.5	1.6	2.75	1.41	--	1.95	--	--
73-3	0.30	87.9	7.0	5.05	3.78	--	1.34	--	--
72-29	0.24	85.0	3.0	4.51	2.39	2.18	1.89	2.07	1.10

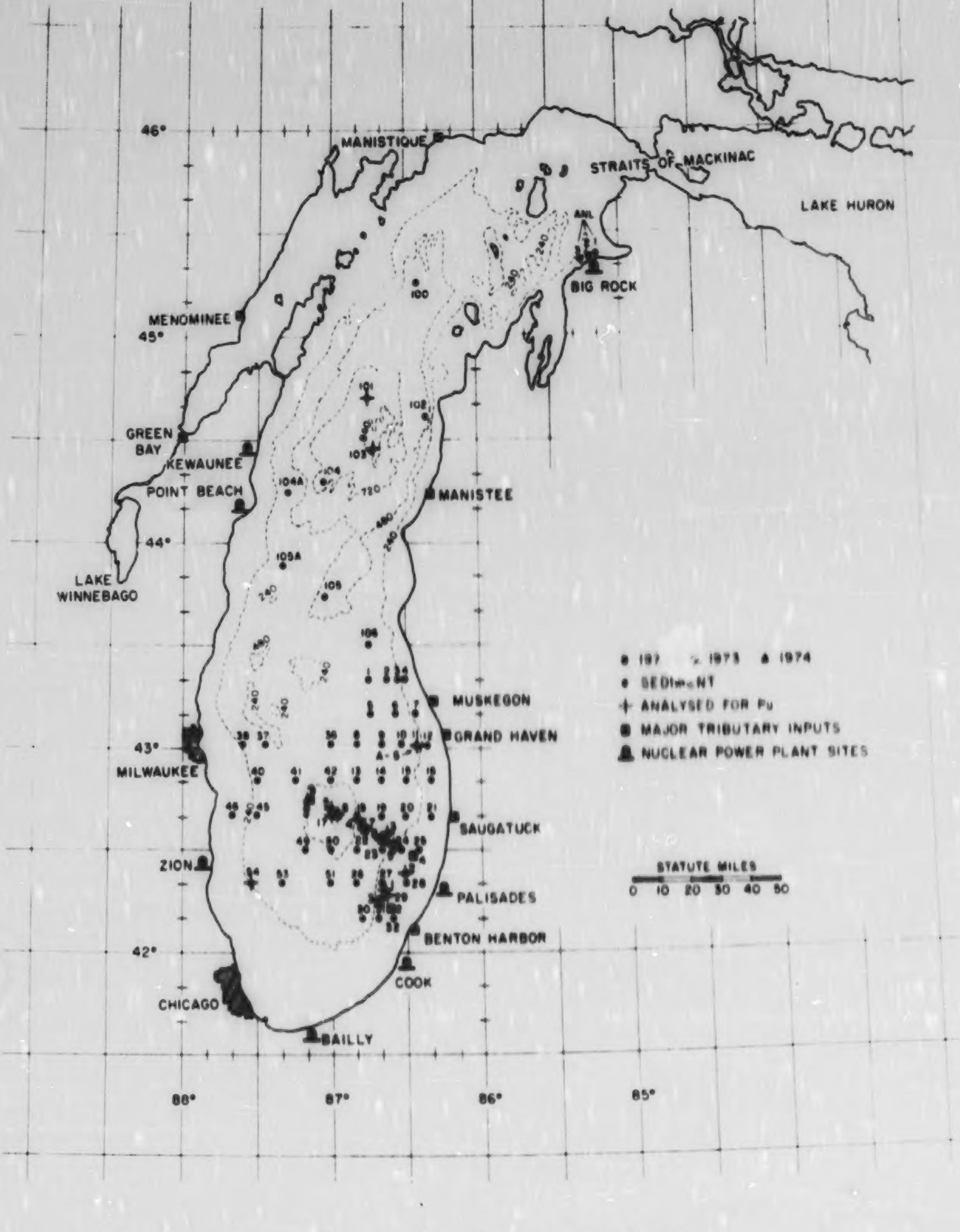
46°
45°
44°
43°
42°
88°
87°
86°
85°
MANISTIQUE
STRAITS OF MACKINAC
LAKE HURON
ANL
BIG ROCK
MENOMINEE
GREEN BAY
KEWAUNEE
POINT BEACH
MANISTEE
LAKE WINNEBAGO
MUSKEGON
GRAND HAVEN
MILWAUKEE
SAUGATUCK
ZION
PALISADES
BENTON HARBOR
COOK
CHICAGO
BAILLY
100
101
102
103
104
104A
105
105A
106
240
480
720
● 197 ☆ 1973 ▲ 1974
● SEDIMENT
✦ ANALYSED FOR Pu
■ MAJOR TRIBUTARY INPUTS
▲ NUCLEAR POWER PLANT SITES
STATUTE MILES
0 10 20 30 40 50

Figure 1. Sampling locations in Lake Michigan.

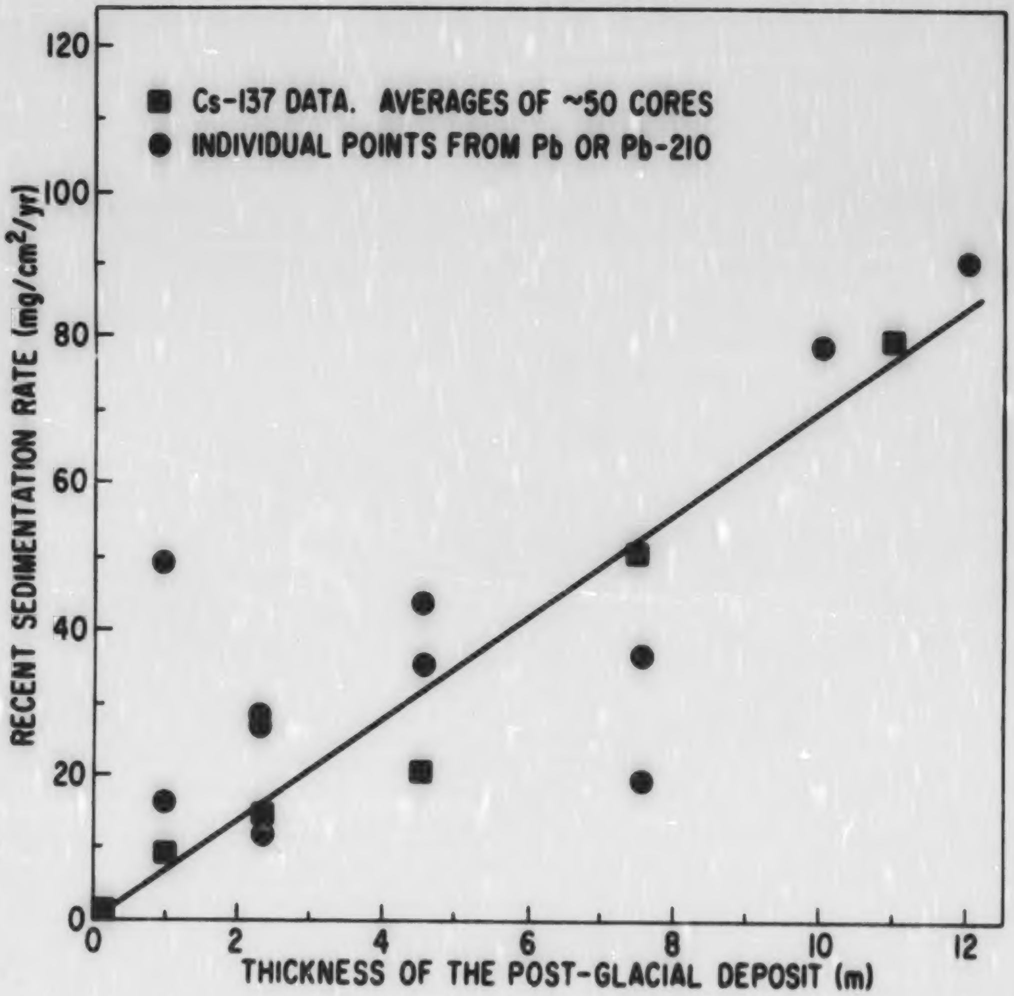

Figure 2. Correspondence between the thickness of post-glacial deposits in Lake Michigan and modern sedimentation rates inferred from radioactivity measurements.

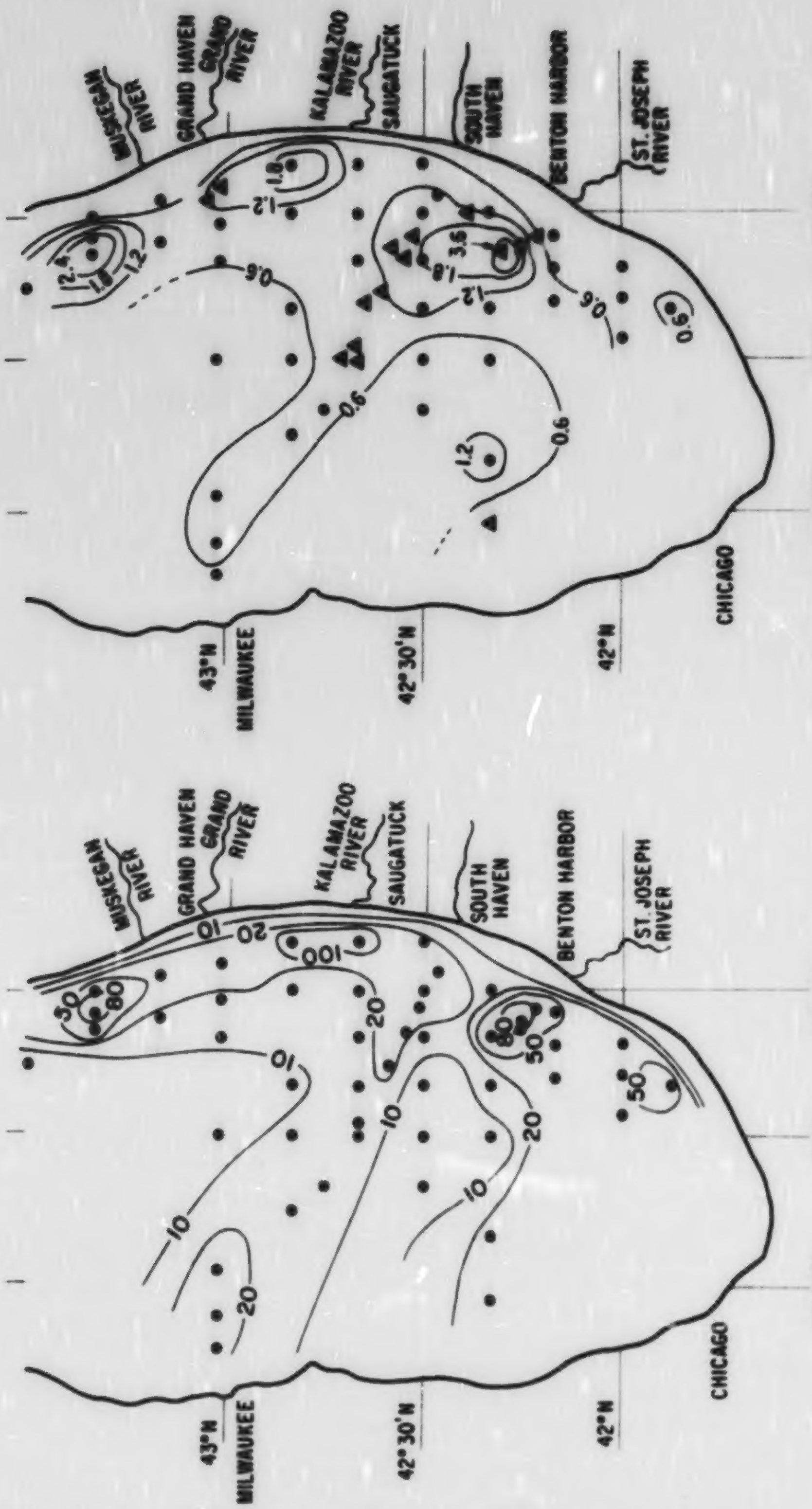
MUSKEGAN RIVER
GRAND HAVEN
GRAND RIVER
KALAMAZOO RIVER
SAUGATUCK
SOUTH HAVEN
BENTON HARBOR
ST. JOSEPH RIVER
CHICAGO
MILWAUKEE
43°N
42°30'N
42°N
87°30'W
87°W
86°30'W
2.4
1.8
1.2
0.6
3.6
10
20
30
50
80
100

Figure 3. Comparison of the mass sedimentation rate and total deposition of ^{137}Cs or ^{239}Pu in southern Lake Michigan. (a) Mass sedimentation rate in mg/cm^2/yr. (b) Total deposition expressed in terms of fCs or fPu (see text).

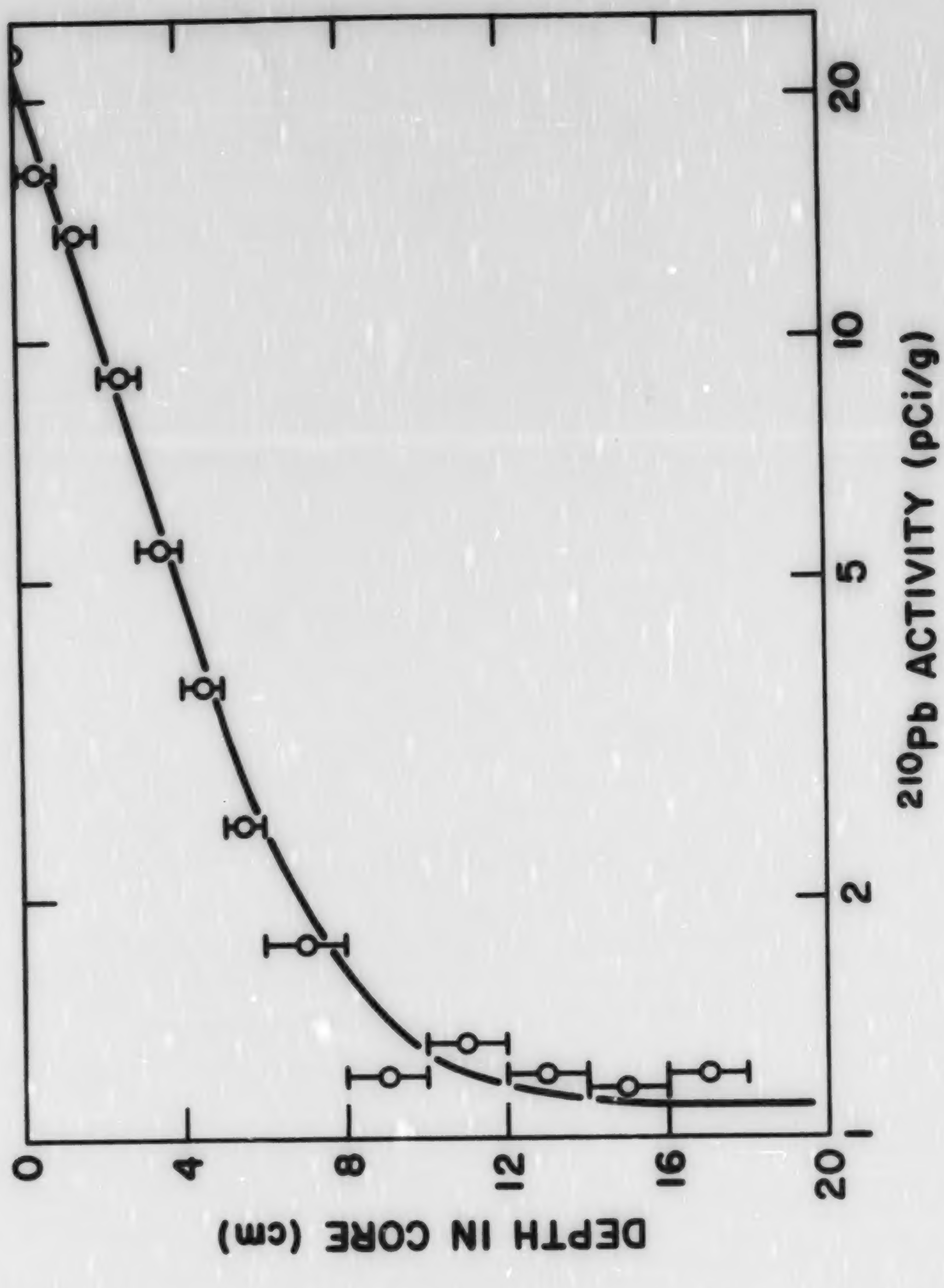

Figure 4. Measured and calculated ^{210}Pb profile at Station 72-103.

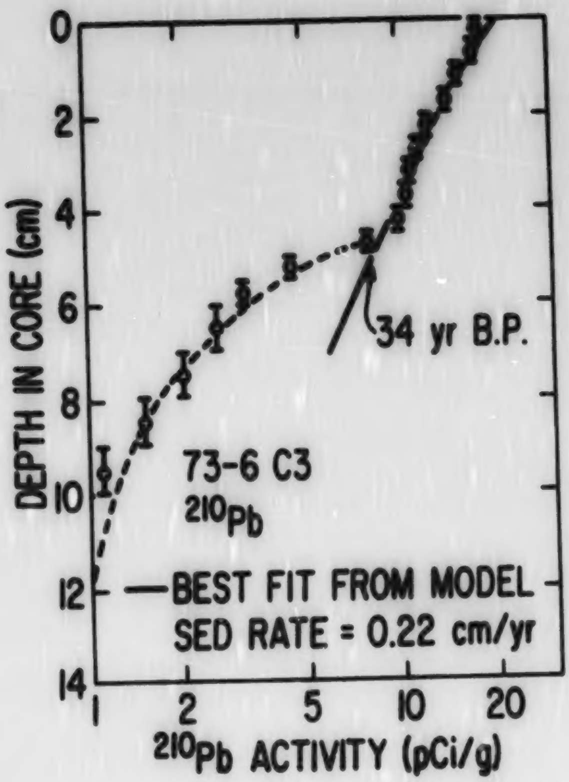

Figure 5. Measured and calculated ^{210}Pb profile at Station 73-6. Note the sharp break at approximately 34 years B.P. (1940) corresponding to an "erosional" event.

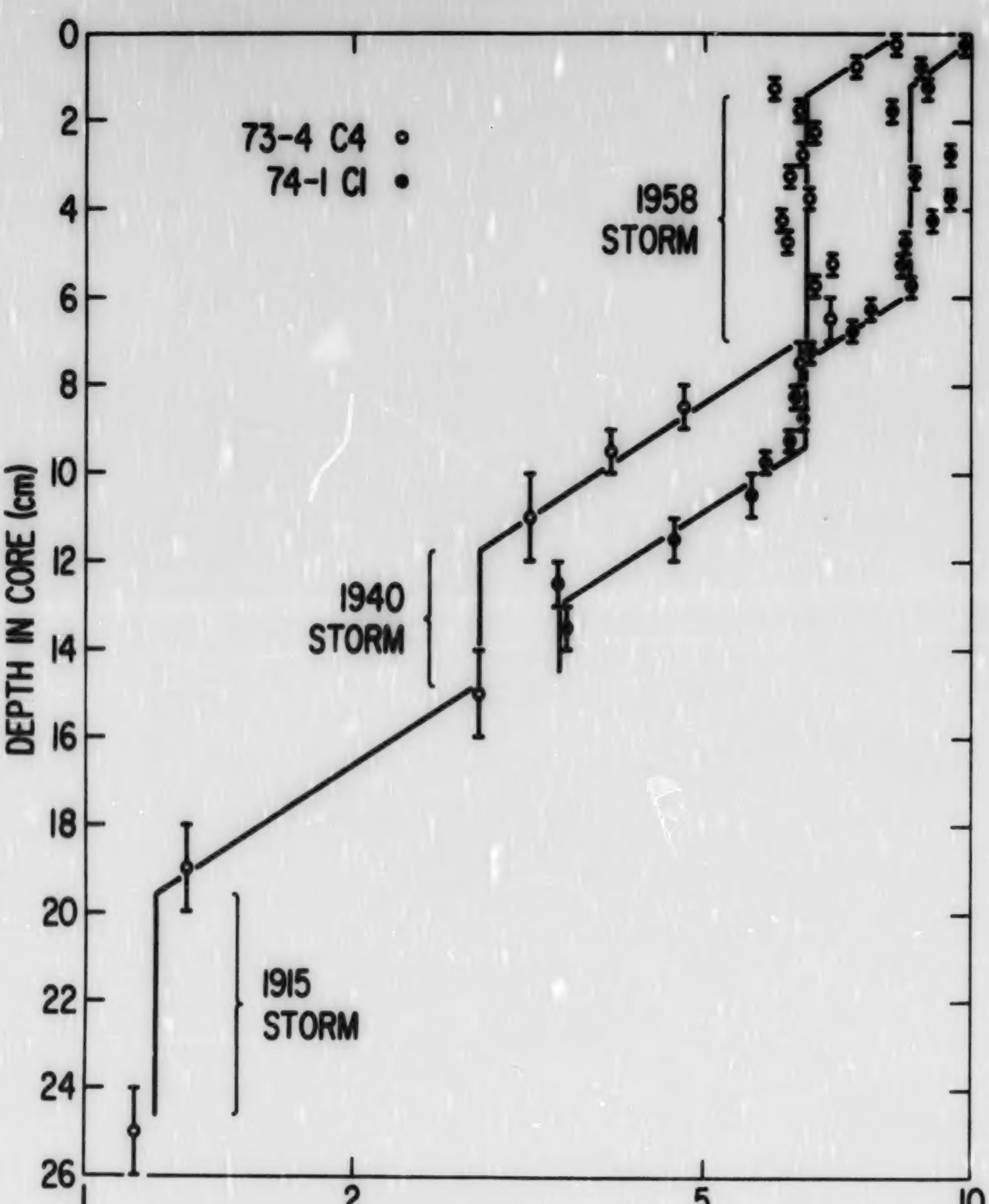

Figure 6. Measured profiles of ^{210}Pb at Stations 73-4 and 74-1. Note the periods of "infinite" sedimentation rate corresponding to the years 1958, 1940, and 1915, interspersed with an apparent constant sedimentation rate.

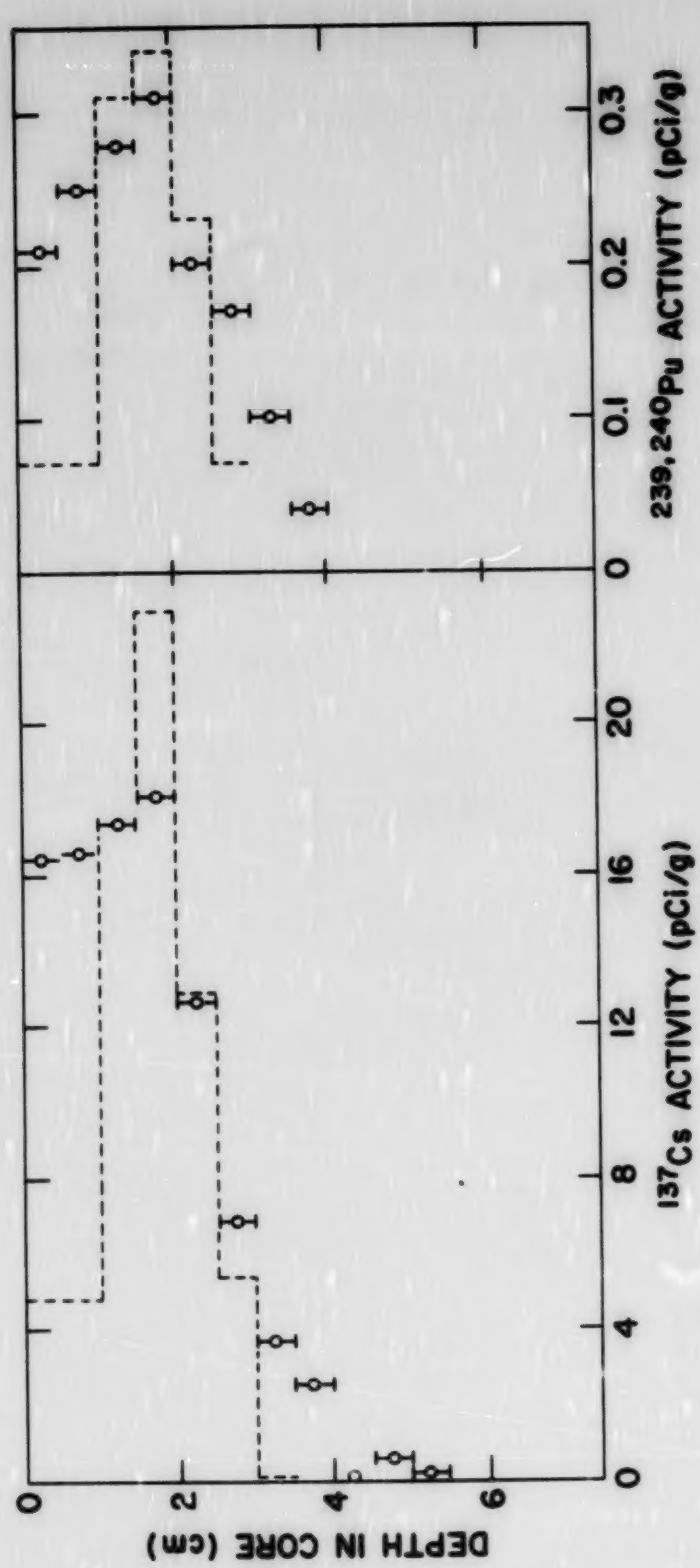

Figure 7. Measured and calculated ^{137}Cs and ^{239}Pu profiles at Station 73-5. Note the difference between the calculated and observed concentrations near the surface. The sedimentation rate is 0.17 cm/yr and there is no surficial mixing.

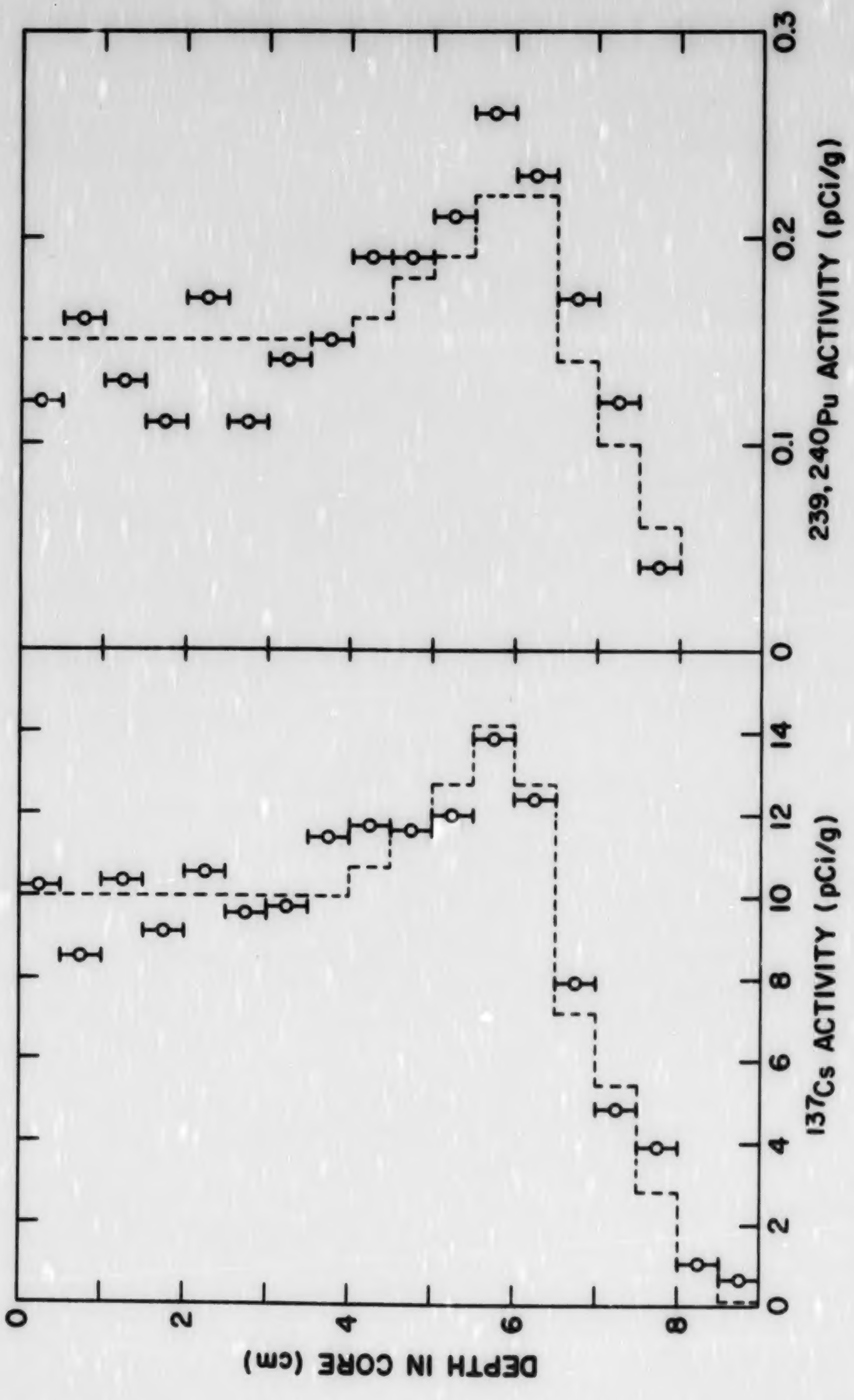

Figure 8. Measured and calculated ^{137}Cs and ^{239}Pu profiles at Station 74-1. The sedimentation rate is 0.5 cm/yr and there is mixing to a depth equivalent to 12 years of deposition.

REACTION RATES OF ELECTRON PAIR DONOR MOLECULES WITH POLLUTANTS IN WATER

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Pollutants in water often are compounds which react with electron pair donors; the latter have also been termed bases and nucleophiles in several contexts. Further, there is a close relationship of donor reactivity to reducing capability. It is possible to convert pollutants to less harmful compounds by reacting them with donors, thus advantage should be taken of donor reactivity in pollution control whenever possible. It is necessary to have some knowledge of the pollutant and of donor reactivity scales in order to choose the proper anti-pollutant. Fortunately, enough data are now available in the literature to make feasible the estimation of a rate for the reaction

$$D + R{-}X \rightarrow D{-}R + X$$

where D is a donor and R-X is a pollutant (hereafter substrate). Even if the exact molecule R-X has not been studied, a range of compounds useful as models have been investigated. It is now possible to predict which donors are very reactive towards model substrates of a general class thus enabling a chemist to confine his study to those donors which are already known to be reactive.

For example, the phosphorus anti-cholinesterases (which include some insecticides and nerve gases) react rapidly with oxygen anions such as hydroperoxide HOO^-, hydroxide OH^- and hypochlorite OCl^- and are unreactive towards donors like iodide ion I^- and thiorea $SC(NH_2)_2$. Minor differences between orders of reactivity of donors towards two tetrahedral phosphorus substrates are to be expected but anything like a complete inversion is not to be expected. In fact, it has been found that hydroperoxide ion is about one hundred fold more reactive than hydroxide for a large number (at least 16) of phosphorus compounds.

Reactivity orders for donor reactions with a number of diverse substrates have been obtained in recent years. Among these are tetrahedral carbon (as in methyl bromide) trigonal carbon (as in esters, carbonium ions, aromatic compounds and olefins), digonal carbon (as in benzonitrile and cyanogen halides), tetrahedral phosphorus, a mixed bag of sulfur compounds, electrophilic oxygen (in peroxides and hypohalites), square planar metal complexes (such as $PtCl_4^{2-}$) and trigonal nitrogen (as in NH_2Cl). Lesser complete sets of data have been reported for boron, fluorine and other halogens, silicon and some octahedral metal complexes. Thus there are sufficient data on compounds that could be acceptable models for almost any pollutant that interacts with donors.

Treatment of donor reactivity is usually accomplished by the technique of linear free energy relationships. These are empirical plots of log rate constant towards one substrate against log rate constant towards another substrate (or rate constant against equilibrium constant, or equilibrium constant against equilibrium constant) with each point on the plot representing two constants for a particular donor. A number of the relationships including those devised by Brönsted, Hammett, Swain and Scott, Edwards and Ritchie will be shown. The correlations of donor reactivity with basicity to protons, with electrode potential, with polarizability and with other scales will be pointed out. The emphasis will be on the experimental observations that are useful in predicting reactivities. (The fundamental basis of reactivity is still to a significant degree unknown so that the practical applications of donor reactivity in pollution treatment are better treated at the semi-empirical level.)

The qualitative terminology (Hard and Soft Acids and Bases) of Pearson will be used to describe the fact that some substrates react with donors following the reactivity order $I^- > Br^- > Cl^- > F^-$ (using halide ions as representative donors) whereas for other substrates the order is $F^- > Cl^- > Br^- > I^-$. More quantitative treatments of the same behavior will also be described, and it will be demonstrated that no less than three parameters are necessary in order to explain donor reactivity. The nature of the alpha-effect and its importance in pollution control will be delineated.

Towards a wide variety of compounds, the hydroperoxide ion is a very reactive donor indeed. Although it is much less basic to protons than is hydroxide ion, it reacts more rapidly in any bimolecular displacement situation (with the probable exception of general base catalysis). In his analysis of donor attack at trigonal carbon centers, Ritchie has found that OOH^- is 2000 fold more reactive than OH^-. The factor is 700 in case of cyanogen chloride (a digonal carbon substrate) and is 35 in the case of benzyl bromide (a tetrahedral carbon substrate). Oxidation of sulfur dioxide by peroxide is very rapid and at least in some pH ranges the attack is by peroxide first acting as a donor, with a subsequent intramolecular redox process. Peroxide can, of course, act as an electrophile (an electron pair acceptor, an oxidizing reagent) and it shows considerable selectivity in control of sewage order, etc.

A number of books contain discussions of donor reactivity. These include texts and monographs in the areas of physical-organic chemistry (Hammett, Ingold, Gould, March, Hine, Kosower), inorganic mechanisms (Basolo and Pearson, Langford and Gray, Edwards), proton reactions (Bell), hard and soft acids and bases (Pearson), enzyme catalysis (Jencks, Bender), bioorganic mechanisms (Bruice and Benkovic, Hudson), linear free energy relationships (Wells, Leffler and Grunwald), and solvent-donor interactions (Amis, Coetzee and Ritchie).

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PHOTOSENSITIZED OXIDATION IN SOLUTION

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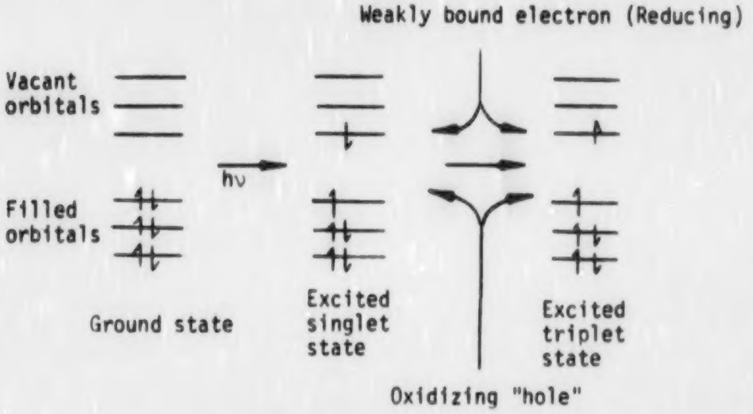
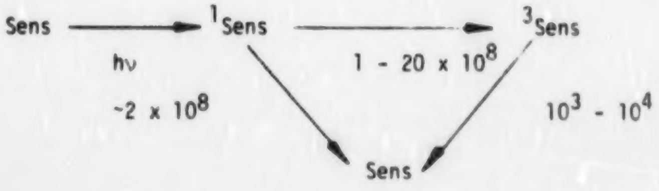
Organic molecules are converted to chemically reactive electronically excited states on absorption of light. Only light that is absorbed can cause photochemical reactions. Absorption of light promotes an electron to a higher orbital without change of spin; thus, the first state formed is the singlet, in which there are no unpaired spins. The singlet in many cases undergoes a spin inversion very rapidly to give the triplet state (which has two unpaired electrons). Usually the triplet state lasts much longer than the singlet. Both states involve electrons promoted to higher orbitals; as these orbitals bind the electrons less strongly than do those of the ground state, one would expect that electrons in these orbitals would be more readily removed by oxidizing agents than would those in the ground state. By the same token, the holes left by the promoted electron are in orbitals that bind electrons comparatively strongly; thus, one would expect that the excited molecule that results would be more readily reduced than the molecule in the ground state. Both expectations are realized: Excited singlet and triplet molecules are both oxidized and reduced more readily than ground-state molecules.



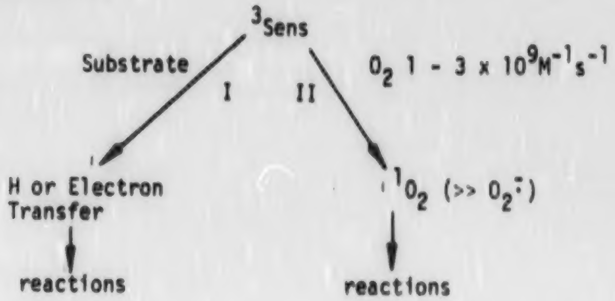
Photosensitized oxygenations of organic compounds have been studied for many years. (1-3) Recent studies have led to greatly increased understanding in this area. It is now possible to recognize several distinct mechanistic pathways, and to make a beginning in predicting which mechanism will occur in a given case. (4,5)

With few exceptions, sensitized oxidations proceed via the sensitizer triplet state, at least in part because the lifetime of the triplet is much longer than that of the singlet. (1-5) The most effective sensitizers are those that give a long-lived triplet state with high quantum yield. Many dyes, such as methylene blue or eosin, natural pigments (chlorophyll, hematoporphyrin, flavins), and aromatic hydrocarbons (rubrene, anthracene), are effective sensitizers. Most of these compounds absorb visible or near ultraviolet light. Typical rates for various sensitizer processes (in $M^{-1}sec^{-1}$) are given below. (5)



Mechanistic Classification

There are two broad classes of reaction open to the sensitizer triplet. (6) The first is one in which the sensitizer interacts with another molecule directly, usually with hydrogen atom or electron transfer. The radicals thus formed undergo further reaction with oxygen or other organic molecules. This reaction has been classed Type I by Gollnick. (1) The second class of reaction, Type II, is one in which the sensitizer triplet interacts with oxygen. The most common of the Type II interactions has been shown to be energy transfer to give singlet molecular oxygen, which reacts further with various acceptors in solution. (7,8) Less efficiently, in the studied cases, electron transfer to oxygen occurs with the formation of the superoxide ion ($O_2^{\cdot-}$); this reaction occurs in less than 1 percent of the deactivating collisions of oxygen with the sensitizer triplet. (9) These reactions are shown below.


^{3}Sens
Substrate
I
II
O_2 1 - 3 x $10^9 M^{-1}s^{-1}$
H or Electron Transfer
$^1O_2$ (>> $O_2^{\cdot-}$)
reactions
reactions

The rates of reaction, k_I and k_{II}, of the two processes are now well enough known that many of the factors governing them can be stated definitively. The rate of the Type I process depends on the sensitizer and the substrate and varies over a wide range. (5)

In general, the types of molecular structure that favor Type I (substrate-sensitizer) chemistry are those that are readily oxidized (phenols, amines, etc.) or readily reduced (quinones, etc.). Compounds that are not so readily oxidized or reduced (olefins, dienes, aromatic compounds) more often favor Type II reactions; however, Type II reactions of amines (10), phenols (11), and other substrates are also known. The rates for the Type II process depend mainly on the oxygen concentration in solution, since the rate constant (k_{II}) with few exceptions falls in the range 1 - 3 x 10^9 $M^{-1}s^{-1}$ for all sensitizers. (1,5) Thus, for example, oxygen is much less soluble in water than in most organic solvents, so that in studies carried out in water saturated with air, the product $k_{II}[O_2]$ is much smaller than in organic solvents saturated with oxygen, as shown in Table 1. Unfortunately, biologists have tended to favor studies under the former set of conditions, whereas most mechanistic chemical studies have been carried out under the latter.

TABLE 1. Rates of Type II Process[a]

Condition	$k_{II}[O_2]$, s^{-1}
Water saturated with air	~5 x 10^5
Organic solvent saturated with oxygen	~2 x 10^7

[a] Assuming k_{II} ~2 x 10^9 $M^{-1}s^{-1}$

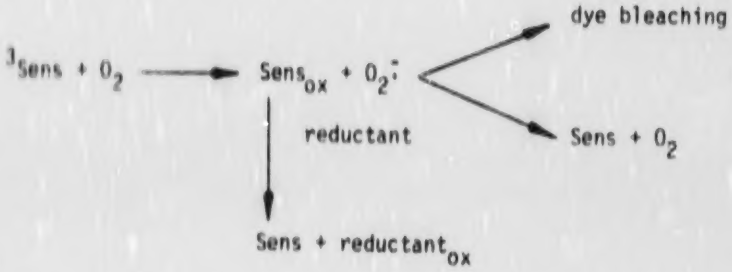
The significant competition that determines whether Type I or Type II reaction occurs is thus between substrate and oxygen for triplet sensitizer. Table 2 shows that, for benzophenone in oxygen-saturated ethanol, the Type I process (with solvent ethanol) competes effectively with the Type II process; however, with eosin under the same conditions, the Type II process predominates and would continue to predominate even at very low oxygen concentration. It is probable that the same is true for bilirubin. Thus, changes in sensitizer, substrate, or concentrations of substrate and oxygen may change the mechanism of the photooxidation from Type I to Type II. It is also important to recognize that binding of dye to macromolecular substrates is likely to favor Type I mechanisms. (12,13)

TABLE 2. Competitive Rates of Type I and Type II Processes for Triplet-State Sensitizer in Ethanol

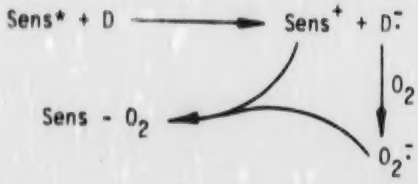
	Rates of Reaction by Type, sec^{-1}	
Sensitizer	$k_I[S]$	$k_{II}[O_2]$
$(C_6H_5)_2C{=}O$	$\sim 10^7$	$\sim 2 \times 10^7$
Eosin	$\sim 10^3$	$\sim 2 \times 10^7$

Products of the Reaction

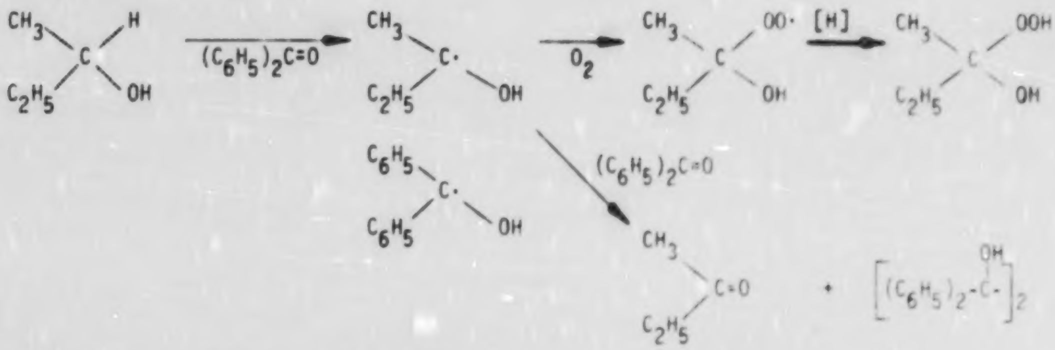
Type I chemistry usually involves the production of free radicals or radical ions. These radicals have a very wide variety of possible reactions, such as reaction with or electron transfer to oxygen, electron or hydrogen abstraction from other substrates, initiation of chain autoxidation, and recombination. Many apparently simple reactions of this type are found to involve complex sequences of reactions when scrutinized carefully. For example, the oxidized dye formed by electron donation to oxygen or another oxidizing species (including another dye molecule) can oxidize the substrate, regenerating dye and giving a new reactive species capable of further reaction or recombination with reduced primary oxidant. (9,14)



Alternatively, an electron donor can react with a sensitizer, giving a radical pair which can react further, as shown below. This reaction occurs well with singlet sensitizers which are electron poor. (15)



Shown below are two examples of Type I reactions: the oxidation of alcohols by benzophenone, which can lead either to ketone or hydroxyhydroperoxide, depending on the conditions (16), and the oxidation of amines, which may proceed either by hydrogen or electron transfer. (17)



$R_2N\text{-}CH_3 \rightarrow \rightarrow R_2NCHO \longrightarrow R_2NH$

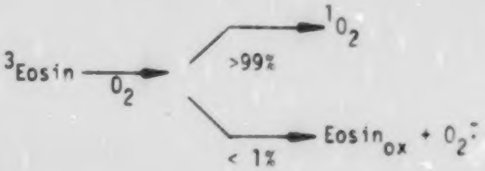
The type II reaction produces singlet molecular oxygen as the primary reactive species. (7,8) There are two excited states of singlet oxygen. The lower energy state, $^1\Delta_g$, is now believed to be the only singlet oxygen species that is reactive. The lifetime of $^1\Delta_g$ oxygen has recently been determined by direct methods and is moderately subject to influence by solvent. The lifetime is shortest in hydroxylic solvents: In water, the lifetime is about 10^{-6}s. (18-19) In aprotic solvents, and particularly in those with no hydrogens whatever, the lifetime is longer and reaches several hundred microseconds.

There is thus a second competition, between the decay rate of singlet oxygen and the product $k_A[A]$; if $k_A[A] << k_d$, the main result of a Type II reaction is simply the quenching of triplet sensitizer, and one may observe no reaction at all. Rates for some typical substrates are given in Table 3.

TABLE 3. Rates of Reaction of Some Typical Substrates with $^1O_2$

Acceptor	k_A, $M^{-1}s^{-1}$
2,5-Dimethylfuran	1.4×10^8
2,3-Dimethyl-2-butene	5×10^7
2-Methyl-2-pentene	1×10^6
1-Methylcyclohexene	2×10^5
Cyclohexene	3×10^3
trans-4-Methyl-2-pentene	3×10^3

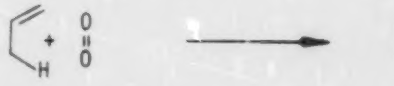
Certain dyes that are less efficient oxidizers can also transfer an electron to oxygen, giving an oxidized dye molecule and superoxide ion. (9,20) For example, eosin reduces oxygen on a small fraction (<1%) of quenching collisions; the other collisions give singlet oxygen.

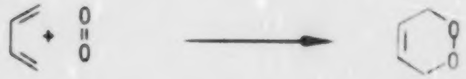


Both oxidized dye and superoxide can react further. Superoxide reacts with alkyl hydroperoxides and H_2O_2 to give reactive radical species capable of inducing autoxidation. (21)

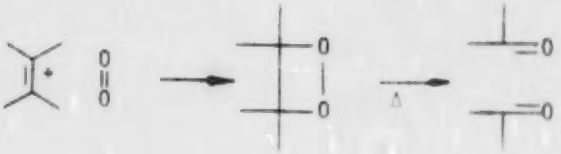
$$O_2^{\cdot -} + ROOH \longrightarrow RO\cdot + OH^- + O_2$$

Two classes of reaction of singlet oxygen are particularly important: addition to olefins, giving allylic hydroperoxides, analogous to the Alder "ene" reaction of Eq. (1), and additions to diene systems to produce endoperoxides, analogous to the Diels-Alder reaction of Eq. (2). (2,22)


(1)


(2)

To these should be added two other classes of somewhat less generality, a 2 + 2 cycloaddition to electron-rich olefins (e.g., enamines and vinyl ethers) and a very few other olefins to produce dioxetanes [Eq. (3)], which are sometimes of moderate stability but readily cleave into two carbonyl-containing fragments (23-25), and oxidation of certain heteroatoms, notably sulfur and phosphorus [Eq. (4)], a reaction exemplified by the oxidation of diethyl sulfide to diethyl sulfoxide, in which two moles of sulfoxide are formed for each mole of oxygen consumed. (26)


(3)

$$2(C_2H_5)_2S + {}^1O_2 \longrightarrow 2(C_2H_5)_2\overset{+}{S}\text{-}\overset{-}{O} \qquad (4)$$

Under ordinary conditions (dye sensitizer, oxygen-saturated in organic solvent, dilute substrate), Type I mechanisms do not occur for these types of substrate. Certain phenols and amines have also been shown to react with singlet oxygen; these reactions may well involve hydrogen or electron abstraction by singlet oxygen, and the overall chemistry resembles that observed in Type I cases. (10,11) Amines and phenols can also quench singlet oxygen; the mechanism of this quenching may also involve electron transfer. (10,11) Carotenes and other highly conjugated compounds with low triplet energies appear to quench by an energy transfer mechanism. (27,28)

$${}^1O_2 + D \longrightarrow D^+ \ldots\ldots O_2^{\cdot -} \longrightarrow DO_2 \quad \text{(reaction}$$

$$\phantom{{}^1O_2 + D \longrightarrow D^+ \ldots\ldots O_2^{\cdot -}} \searrow D + {}^3O_2 \quad \text{(quenching)}$$

$${}^1O_2 + \text{carotene} \longrightarrow {}^3O_2 + {}^3\text{carotene} \longrightarrow {}^3O_2 + \text{carotene} \quad \text{(energy transfer)}$$

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CHEMICAL DEGRADATION OF ORGANIC POLLUTANTS IN THE ENVIRONMENT

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Soil becomes the ultimate residence of a great deal of the organic pollutants that may be released into the environment. It also receives quantities of a wide variety of organic compounds that arise out of natural systems. The synthetic chemicals may be industrial effluents, waste products, or chemicals that have been used as pesticides. Detailed studies have shown that a variety of things can happen to the chemical once it reaches the soil. The chemical may be further transported by leaching or soil erosion or even by evaporation from the soil surface. Almost certainly, any chemical in intimate contact with the soil will be sorbed to a greater or lesser degree by one of the fractions.

Once in the soil, the organic pollutant is subject to a number of physical, chemical, and biological processes. It may undergo complexation, be subject to chemical reactions, or be modified and degraded by a series of biochemical reactions mediated by organisms or extra-cellular enzymes. This presentation is primarily concerned with certain of the physical and chemical reactions in soil leading to degradation, excluding the redox reaction which is the subject of another presentation.

Among the pollutants, the pesticides and their degradation have been the most extensively studied in soils. Consequently, many of the examples used are those of pesticides, but this poses no serious limitations. Many organic groupings are represented among the pesticides, thus providing appropriate models for a number of organic compounds from other sources.

In considering the non-biologically mediated reactions of organic pollutants in soil, we are left with the photochemical and the chemical. For obvious reasons the photochemical reactions are probably of little significance in degradation of organic pollutants once the chemical has entered the soil. Indeed, once sorbed even at the surface of the soil, photochemical degradation is probably slow. The importance of chemical reaction including coordination or complexation may be of variable importance depending on the nature of the pollutant under consideration. With some compounds, investigators have found the rate of chemical reaction in soil under environmental conditions to be slow compared to the biologically mediated reactions. Thus, for example, while the chlorotriazines are hydrolyzed by soil, the chemical hydrolysis catalyzed by benzoxyazinone is more related to plants since the catalyst is presumed to be a constituent thereof. On the other hand, certain of the organophosphorus insecticides have been shown to undergo hydrolysis that is catalyzed by clays. The relative importance then of the purely chemical hydrolysis of an organic pollutant in soil must be determined for the individual compound as there is not yet sufficient data to allow a generalization.

Coordination

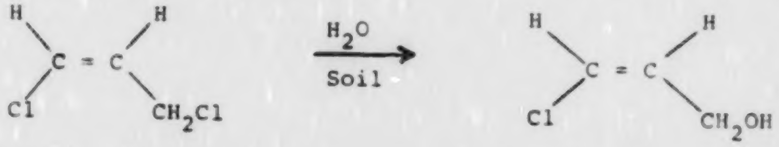
A number of organic pollutants have been shown to react with various cations to form coordination complexes. In some instances, this occurs in solution, in other instances, the coordination occurs at exchange sites on the clay colloid that are occupied by the appropriate element. An example of the first instance is the compound aminotriazole that forms coordination complexes with certain of the transition elements such as nickel, cobalt, and copper. The alkyl amines on the other hand, coordinate with the element located on a reactive site of clay complexes.

Certain elements present in the soil or added as an amendment may serve as a catalyst in the degradation of pollutants. It has been found that magnesium oxide catalyzes the dehydrochlorination of DDT to DDE.

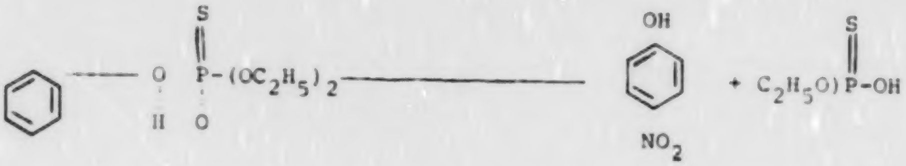
CHEMICAL DEGRADATION OF ORGANIC POLLUTANTS IN THE ENVIRONMENT
continued

Hydrolysis and Other Nucleophilic Reactions

Perhaps the most extensively studied chemical reaction leading to degradation of organic pollutants is that of hydrolysis. A number of compounds are sufficiently reactive to undergo hydrolysis including the halogen substituted alkanes and alkenes, esters, amides, anhydrides, and epoxides. The soil fumigant, 1.3-dichlorpropene is hydrolyzed in soil to either cis- or trans- 3-chloroalylalcohol as shown in the following reaction:



The organophosphorus insecticides have perhaps been the most extensively studied group of organic pollutants as regards hydrolysis in soil. Parathion (o,o-diethyl paranitrophenyl phosphorethiolate) has been shown to undergo slow hydrolysis even on dry soil.



That the soil is important in the hydrolysis of the organophosphorus chemicals is illustrated by the much more rapid rate of hydrolysis of malathion in soil than in aqueous solution.

Other types of compounds shown to undergo hydrolysis included the n-methyl carbamates in which the half-life of the 4-N-methyl benzothienyl carbamate was shown to be something under 8 days at 20°C. The esters of carboxylic acids such as the esters of 2,4-D undergo rapid hydrolysis in soil.

Factors Influencing Rates of Hydrolysis

As would be expected in so complex a system as the soil, a number of factors are operative in determining the rate of hydrolysis. At a given moisture content the most important factors appear to be temperature and pH of the soil. Other rate determining factors include the soil type, the nature of the clays present, the ions, e.g. alkali and alkaline earth cations, salt concentration, and the concentration of the pollutant.

Only limited studies have been performed in measuring actual reaction rates and determination of the apparent odors of the hydrolysis reaction in soil. Obviously, with the complexity of reactions, it is difficult to separate the biologically mediated reactions from the chemical reactions except by heat or radiation sterilization of the soil. However, with some of the compounds studied the pseudo first-order kinetics appears to describe rates reasonably well. With a few compounds, notably the chlorinated picolinic acid, picloram, a hyperbolic law appears to best describe the observed rates.

Chemical reactions, notably hydrolysis, coordination, oxidation and reduction, play a role in degradation of organic pollutants in soil. Though the rates are not always comparable to the biologically mediated reactions, nonetheless, the chemical reactions probably play an important role in degradation. There has not been sufficient study of the purely chemical reactions in degradation of organic pollutants to give an intimate understanding of their importance with all classes of compounds. This is an area warranting much more research in the future.

Solar Spectral Irradiance Reaching the Ground

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1. Introduction

I will present some illustrative results of intensive calculations carried out to assist scientists concerned with the biological consequence of ultraviolet radiation. These results are given in the form of practical "engineering formulas" which give ground based UV spectral irradiances, dose rates, daily doses, and annual doses for various atmospheric models, locations and time of year. While the results are specialized to the 280-340 nm spectral region, the formulas can also be applied to other spectral regions with an appropriate readjustment of parameters.

2. Elementary Concepts of Atmospheric Transmission

The calculation of solar radiation reaching the ground has many aspects which are familiar to radiation physicists, photobiologists, and many other scientists. Essentially the sun is the radiation source, the atmosphere is the propagating medium, which absorbs, diffuses, or in some cases reemits radiation, and people, animals, plants, or instruments serve as detectors.

Let us first consider the simplest aspect of the atmospheric radiative transfer, namely the law of attenuation, variously attributed to Beer, Lambert or Bouguer. Suppose we have a collimated beam of monoenergetic incident light particles with the intensity I (photons/cm^2 sec). We introduce into this beam a thin (Δw) layer of substance having n molecules/cm^3. If these molecules interact with the incident beam, the transmitted beam intensity will be reduced by the effective area blocked out by the $n\Delta wA$ molecules in the beam. If the reduction in intensity is ΔI, we may define an area associated with each molecule by means of

$$\frac{\Delta I}{I} = -\frac{\sigma n\Delta wA}{A} = -\sigma n\Delta w \qquad (1)$$

The number of molecules per cubic centimeter may be calculated using $n = \rho N_a/M_a$, where ρ is the density (in gr/cm^3), N_a is Avogadro's number, and M_a is the gram molecular weight.

The characteristic area σ obtained from such an experiment depends upon the properties of the target molecules, and the nature of the incident light or particles. Our assumption of a thin layer permits us to ignore the overlap of the areas associated with different molecules.

In many types of absorbing processes we may assume that σ is independent of the distance of penetration. This is usually true for light quanta, when spectrally separated at high resolution, and gamma rays and neutrons passing through solids. However, it is not true for infrared radiation measured at low resolution or for charged particles such as electrons and protons, which interact with many scatterers via the long-range coulomb forces. In these latter cases the quality of the beam degrades and hence the value of σ varies with depth. In the former case, i.e. when σ is constant, we may integrate Eq. (1) to obtain

$$I = I_o e^{-\sigma n w} \tag{2}$$

where I_o is the incident intensity and I is the intensity at any depth w in the absorber.

In atmospheric problems the number densities are altitude dependent, hence, we must calculate the total thickness of a column of air above an observer. We may do so using

$$w(y) = \int_y^\infty \rho(y)dy \tag{3}$$

where y is the altitude variable and $\rho(y) = n(y)/n_o$ is the relative density. To allow for the extra thickness, when the look angle departs from the zenith (see Fig.1a), we usually divide w by μ where $\mu = \cos\theta$. This may be called the flat earth approximation. Accordingly the formula for transmission is

$$T = I/I_o = e^{-n_o\sigma w/\mu} = e^{-kw/\mu} = e^{-\tau/\mu} \tag{4}$$

where $k = n_o\sigma$ is the attenuation coefficient and $\tau = kw$ is the optical depth.

When we have several attenuators along a path, the total transmission is simply the product of the transmission function for each attenuator or the optical depth is the sum of the component optical depths. Figure 1b (Green, Sawada, Shettle (GSS), 1974) illustrates the simplest model which can, with some degree of realism, be applied to the problem of attenuation of solar ultraviolet radiation by ozone, air molecules and atmospheric aerosols.

3. The Transmitted Solar UV Irradiance at the Ground

Using the foregoing formulas, the downward component of the transmitted solar irradiance is given by

$$B_t(\theta,\lambda) = \mu H(\lambda) \exp - A_t(\theta,\lambda) \tag{5}$$

where

$$A_t(\theta,\lambda) = \textstyle\sum_i w_i(\lambda)k_i(\lambda)/\mu_i \tag{6}$$

Here $H(\lambda)$ is the extraterrestrial solar flux, θ is the solar zenith angle, i = 1, 2, 3 denote air, particulates and ozone respectively, $w_i(y)$ denote the altitude dependent vertical thickness, $k(\lambda)$ the wavelength dependent attenuating coefficient. To allow approximately for the fact that the earth is round, we use a generalization of $\mu = \cos\theta$ given by

$$\mu_i = [(\mu^2 + t_i)/(1 + t_i)]^{1/2} \tag{7}$$

where t_i are species dependent dimensionless parameters, which keeps μ_i from going to zero at 90°. To a reasonable approximation the extra terrestrial solar irradiance in low resolution in any narrow spectral region may be approximated by a linear relationship.

$$H(\lambda) = K\left[1 + \frac{\lambda-\lambda_o}{d}\right] \tag{8}$$

The parameters K, d and λ_o for the 280-340 nm region are given in Table 1. Note that this formula yields 1 watt/m^2 nm at $\lambda = 330$ nm (see Fig. 2), which might be compared with the integrated solar constant of 1.37 kw/m^2. If we now specify the optical depths of the three components at a standard wavelength and their wavelength dependencies, we can simply calculate the downward transmitted component of the sun's UV irradiance using Eqs. (5) and (6). The spectral dependence of the optical depth for ozone, air and a representative aerosol model in the UV region of interest are illustrated in Fig. 3. These are based upon analytic representations of the attenuation coefficients given by

$$k_1 = k_a(\lambda_o/\lambda)^{\nu_a}, \quad k_2 = k_p(\lambda_o/\lambda)^{\nu_p}, \quad \text{and } k_3 = k_{oz} \exp -[(\lambda-\lambda_o)/d_o] \tag{9}$$

and the thickness vs. altitude functions

$$w_1 = w_{10}\left[\frac{(1+\alpha)}{\alpha+e^{y/h_1}}\right] \tag{10}$$

$$w_2 = w_{20}\frac{(1+\alpha_2)}{\left(\alpha_2+e^{y/h_2}\right)} + w'_{20}\frac{(1+\alpha')}{\left(\alpha'+e^{y/h'_2}\right)} \tag{11}$$

$$w_3 = w_{30} / \left[1+e^{(y-y_3)/h_3}\right] + w'_{30}\, e^{-y/h'_3} \tag{12}$$

Suitable constants for a standard atmosphere are given in Table 1. Figure 4 illustrates the downward transmitted irradiance as a function of the solar zenith angle computed using these equations and parameters.

4. The Diffuse Spectral Irradiance

Prior to 1974, almost all UV spectral irradiance calculations considered only the directly transmitted solar irradiance (i.e. sunlight), but ignored the diffusely scattered irradiance (i.e. skylight). The available UV skylight calculations (Dave and Furukawa, 1966) consider only the case of a purely molecular cloud-free atmosphere. To deal with the turbid atmosphere prevailing over most population centers, we proceeded along several parallel paths. One path (Green, Sawada, Shettle, 1974) was addressed towards developing an analytic representation of the diffuse spectral irradiance in the middle ultraviolet which could serve as a synthesis of the 10-year UV measurement program of Bener(1972). The second path (Shettle and Green, 1974) used a simple and fast multiple scattering calculational technique to obtain the UV skylight component. When completed, this was found to conform reasonably well to our analytic synthesis as well as to the more elaborate multiple scattering calculations of Dave and Braslau (1975). A third path (Mo, Kezwer and Green, 1975) utilized a simple two-stream approximation to analytically represent multistream solutions of the radiative transfer equation. A fourth path (Chai and Green, 1976) involved measurements of the ratio of the diffuse to transmitted components which follows a fairly simple systematics.

According to GSS, the downward scattered irradiance may be represented by the empirical formulas

$$B_s(\theta,\lambda) = H(\lambda)\exp - D_s(\theta,\lambda) \tag{13}$$

where

$$D_s(\theta,\lambda) = L_{ap}/\mu_{ap} + L_{oz}/\bar{\mu}_{oz} \tag{14}$$

$$L_{oz} = K_{oz}\, e^{\kappa k_{oz} w_3 - (\lambda-\lambda_o)/\delta} \tag{15}$$

$$L_{ap} = \ell_o\left[1 + \ell_1 y + \ell_2\, (w_2 k_p - \ell_3)^2\right] \tag{16}$$

where μ_{ap} has the form of Eq. (7) but with

$$t_2 + s_2 = t_{20}\, (1 + t_{21} y)(y \text{ in Km}) \tag{17}$$

and where (with a minor change from GSS)

$$\tilde{\mu}_{oz} = \left[\left(1 - \frac{\sin^p\theta}{q}\right)^{\frac{\lambda-\lambda_o}{\delta p}}\right] \times \left(\frac{\mu^2 + s_3}{1 + s_3}\right)^{1/2} \tag{18}$$

The constants for this equation are also given in Table 1, Figure 5 illustrates the diffuse spectral irradiance based upon these analytic representations of the systematic experimental results of Bener.

The global flux $G(\theta,\lambda)$ can now be obtained by addition i.e.

$$G(\theta,\lambda) = B_t(\theta,\lambda) + B_s(\theta,\lambda) \tag{19}$$

While these formulas are simply empirical representations of experimental data or of ab - initio multiple scattering calculations they can serve the valuable purpose of providing approximate estimates of skylight in a form almost as convenient as that of Beer's law for the transmitted component of sunlight.

5. Irradiances or Dose-Rates

For many purposes we are not interested in the spectral irradiance at the ground but rather the irradiance as measured with a detector or biological system with a given response function (Green, Mo and Miller (GMM) 1974). The specification of the relative efficiency $\varepsilon(\lambda)$ of a detector enables us to translate a spectral irradiance into an irradiance or dose rate. For example

$$\phi_t(\theta) = \int \varepsilon(\lambda) B_t(\theta,\lambda)\, d\lambda \tag{20}$$

is the transmittted irradiance associated with a transmitted spectral irradiance $B_t(\theta,\lambda)$. The units of $\phi_t(\theta)$ is effective-watts/m^2, or $(W/m^2)_e$, a unit which is defined relative to the specific efficiency curve chosen.

For illustration let us choose an analytic representation of the relative erythema spectrum measured by Coblentz and Stair (1934) as the standard $\varepsilon(\lambda)$. In the 280-340 nm region this $\varepsilon(\lambda)$ can be accurately represented by (see Fig. 6)

$$\varepsilon(\lambda) = 4 \exp\left(\frac{\lambda-\lambda_p}{\lambda_f}\right) \Big/ \left[1 + \exp\left(\frac{\lambda-\lambda_p}{\lambda_f}\right)\right]^2 \tag{21}$$

Figure 7 illustrates the results of a numerical calculation of the integral defined by Eq. (21) and the correspond scattered dose rate for a standard atmospheric condition. It should be noted that the erythema dose rate associated with the diffuse flux in this instance is larger than that associated with the transmitted flux.

It is noteworthy that these numerical results can be represented quite accurately by simple analytic functions of angle. For example the global dose rate $\phi_g = \phi_t + \phi_s$ may be represented accurately by

$$\phi_g(\theta) = \mu\, \phi_g(0) e^{\kappa}\, e^{-\kappa/\mu_g(\theta)}\ , \quad \left(\mu = [(\mu^2 + g)/(1 + g)]^{\frac{1}{2}} \right) \tag{22}$$

where μ_g is defined by Eq. 7 (with t → g). The quantity $\phi_g(0)$ equals the value of $\phi_g(\theta)$ at $\theta = 0$ and the parameters κ and g can be obtained by fitting Eq. 22 to the numerical results of the integrations. We have found that these parameters are smooth slowly varying functions of ozone concentrations (see GMM).

6. Daily Dose

The daily dose corresponding to the global irradiance or dose rate may be defined by

$$\Delta = \int \phi_g(\theta)\ dT \tag{23}$$

where $\phi_g(\theta)$ may now be represented by Eq. (22), and the integration with respect to the time of day (T) is from sunrise to sunset. The relationship between the time of day (measured from noon) and latitude (L) and solar declination (D) is given by

$$\mu = \cos\theta = \sin L \sin D + \cos L \cos D \cos T \tag{24}$$

where T the hour angle is measured from the local noon. Using this equation the quantities $\phi_g(\theta)$ and μ_g become implicit functions of time.

We have evaluated many integrals of this form of Eq. (23) and have found it possible to represent the results of such numerical integration quite accurately (1% - 3%) with the formula

$$\Delta = 2c_t\, \bar{\phi}_g \left[\sin L \sin D \cos^{-1}(-\tan L \tan D) + \sqrt{\cos^2 L \cos^2 D - \sin^2 L \sin^2 D} \right] \tag{25}$$

where c_t = 13751 sec/rad converts the hour angle T (in radian) to time (in sec) and

$$\bar{\phi}_g = \phi_g(0) e^{\bar{\kappa}} \left[\frac{\rho + 1}{\rho + e^{\bar{\kappa}/\mu_{\bar{g}}(L-D)}} \right] \tag{26}$$

The best-fit values of $\bar{\kappa}$, and $\bar{g}$ for different amounts of ozone are smooth functions (see GMM) and ρ may be taken as a constant. The results of such a fit to numerical outputs are illustrated in Fig. 8 which shows the latitudinal and monthly variation of the daily erythema dose for standard atmospheric conditions.

6. Annual Doses

The analytic representation of daily dose as a function of solar declination and latitude and the parameters which characterize the ozone distribution and turbidity may be used to calculate the annual dose for any location in terms of the climatological data. Mo and Green (1974) have found that for a cloudless sky the annual erythema dose can be accurately represented as a function of latitude by the analytic expression

$$D_a(L) = B \Big/ \left[1 + e^{(L-L_o)/L_f} \right] \tag{27}$$

where $D_a(L)$ represents the annual erythema dose in effective joules/m^2 or $(\text{joules}/m^2)_e$ at the latitude L (in degrees). The adjustable parameters B, L_o, L_f are obtained by NLLS fitting the numerically calculated results of annual erythema doses. The points in Fig. 9 are the annual erythema doses calculated with the experimentally determined worldwide ozone distribution, which depends on the geographic latitudes and seasons of the year (12) and with an assumed ground albedo of 0.05. The solid curve in Fig. 9 represents the fit to these points with Eq. (27) and the parameters $B = 24.1 \times 10^5\ (\text{Joules}/m^2)_e$, $L_o = 30$, $L_f = 15$. Calculations with a 5%, 10% and 20% reduction of the ozone distribution are also exhibited in Fig. 9. These modified curves can be represented accurately by Eq. (27) with the constant B replaced by

$$B' = B\,e^{\alpha f} \tag{28}$$

where $\alpha = 1.53$ and $f = -\Delta w_{oz}/w_{oz}$ is the fractional depletion of the ozone column thickness (w_{oz}).

If we chose other types of response curves e.g. the DNA absorption spectrum we will obtain results which also can be fit by these equations but with altered parameters.

Calculations on the influence of cloud cover, cloud and smog thickness, ground albedo and local ground elevations (i.e. altitude) upon the annual dose may be approximately accommodated by generalizing Eq. (27) to the form

$$D_a = Be^{\alpha f}\left(\frac{1-\Gamma\, e^{\theta} C_\ell}{1+e^{(L-L_o)/L_f}}\right)\cdot\left(\frac{e^{h/H - \tau_s/\tau_{so}}}{1 - r_o A}\right) \tag{29}$$

where $H = 8$ Km, $\tau_{so} = 4.2$, $\Gamma = 0.056$, $r_o = 1/3$

$$\theta = \sqrt{\tau_c/\tau_{co}} - 1 \text{ with } \tau_{co} = 15.$$

The denominator of the first factor allows for the latitude dependence of the annual erythema dose. The numerator of the first factor allows for the cloud cover (C_ℓ) and cloud thickness (τ_c) and is based upon the work of Buttner (see Cutchis (1973) and Nack and Green (1974). Values of C_ℓ (measured in tenths from 0-10) for many metropolitan areas can be obtained from the Climatic Atlas (NOAA, 1969; see also MG). Unfortunately data does not appear to be available on cloud thickness. The denominator $(1-r_oA)$ in the second factor corrects for the ground albedo (A) where r_o is an approximate air-ground-air reflection coefficient for the solar radiation in the 300°- 320 nm interval (2). Values of A can be as large as 0.75 for snow conditions. The factor $e^{h/H}$ represents the influence of local ground altitude, (h) as suggested by the results of Bener (1972). The factor $e^{-\tau_s/\tau_{so}}$, where τ_s is the smog optical depth at ~305 nm, is a correction suggested by the results of Nack and Green (1974).

The same correction factors shown in Eq. (29) may be used in daily dose rate or spectral irradiance calculations as an approximate basis for allowing for cloud cover, smog, etc. In most cases the uncertainty in climatological data is the primary limitation on the accuracy of the predicted results.

7. An Application of Dose Calculations

Our approximate methodology for assigning dose may be used for a variety of applications. For example one might attempt to correlate the calculated annual doses with reported skin cancer incidence rates (Green and Mo, 1974, Green et al 1976). Figure 10 illustrates such a correlation for two sets of non-melanoma skin cancer data (1) older data in the literature from the United States, United Kingdom, Canada and Australia (points) and (2) recent data from the recent Third National Cancer Survey (circles). Also shown are best fit curves satisfying the functional form

$$R = R_o e^{D/Do} \tag{30}$$

While the values of R_o differ for the two sets of data it is interesting to note that the same e folding dose $Do \sim 0.33$ can be used for both. This is important since such a non-linear dose response curve implies a varying relationship between an percentage increase in dose and the corresponding percentage increase in incidence rate i.e.

$$\beta = (dR/R) \ / \ (dD/D) = D/Do \tag{31}$$

For example for Northern U.S.A. $(D \sim .4)$ $\beta \sim 1.2$; for Central U.S.A. $(D \sim .7)$ $\beta \sim 2.1$ whereas for Southern U.S.A. $(\beta \sim 1)$ $\beta \sim 3$.

A number of other applications of our spectral irradiance, dose rate and dose calculations to other biological systems have been made (Nachtwey Ed. 1975 Vol 5 CIAP)

8. Summary and Conclusion

The subject of atmospheric radiative transfer is now undergoing very rapid development and the literature is expanding at a fast pace (see Coulson, Fraser, 1975). Theoretical work in this field usually requires the use of large computers to solve the complex integrodifferential equation of radiative transfer. The influence of clouds, smog, and other climatologial variables upon calculated irradiances has just been explored and much work remains. Experimental work is frought with many technical problems and it is quite difficult even under clear sky conditions to measure spectral irradiance or integrated irradiance with accuracies better than 5%. It is very difficult to characterize the influence of clouds upon spectral irradiance measurements in any organized way.

For these various reasons there tends to be a large gap between atmospheric radiative transfer specialists and persons who need to know atmospheric radiation levels for various applied problems. The formulas presented in this report were developed for the purpose of bridging the gap in the important spectral region extending from 280 nm - 340 nm. From a number of exploratory calculations however, we have become convinced that these formulas can be adapted to serve in a much larger contex mostly by a simple readjustment of the parameters.

The author would like to thank his many collaborators for their assistance in these endeavors and the National Science Foundation and the Department of Transportation for their support.

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Table 1

Constants Associated with Transmitted and Diffuse Flux

Air (1)	Particulates (2)	Ozone (3)	Diffuse
w_{10}=8.423 Km	w_2=1.404 Km	w_3=0.32 cm	L_{ap}=0.873
k_a =0.145 Km^{-1}	k_p=0.260 Km	k_{oz}=10 cm^{-1}	K_{oz}=1.32
ν_a =4.27	ν_p=0.58	t_3 =0.0074	κ =0.277
t_1 =0.0018	w_{20}=1.40 Km		δ =7.70 nm
λ_o =300 nm	h_2 =1.0 Km	d_o = 8 nm	p =3.887
h_1 =6.42 Km	α_2 =0.4	w_{30}=0.304 cm	q =1.269
α =0.312	w_{20}'=0.0045 Km		s_2 =0.06
	h_2'=2.5 Km		s_3 =0.12
K=0.552 $\frac{\text{Watts}}{m^2\text{-nm}}$	α' =2981	y_3=23.2 Km	ℓ_o =0.872
			ℓ_1 =0.179
d = 37 nm	t_2 =0.0003	h_3=4.63 Km	ℓ_2 =0.0487
		w_{30}'=0.0177 cm	ℓ_3 =0.538
		h_3' =5.78 Km	t_{20}=0.06
			t_{21}=1.867

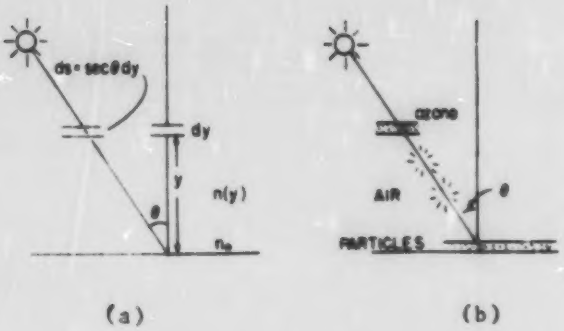


Fig. 1 Schematic illustration of the direct solar irradiance reaching the Earth's surface. (a) geometry (b) transmission through ozone, air and aerosol layers (adapted from GSS)

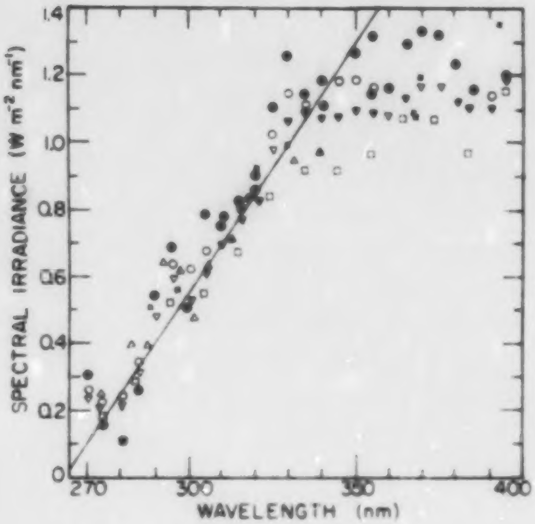


Fig. 2 Plot of reduced measurement points from pertinent references (see GSS). The straight line represents Eq. (8) (adapted from GSS).

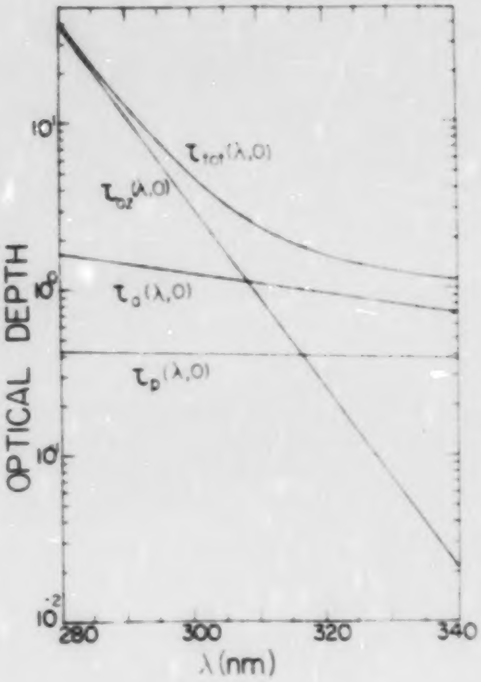


Fig. 3 Optical depths of atmospheric constituents as a function of wavelength (adapted from SG).

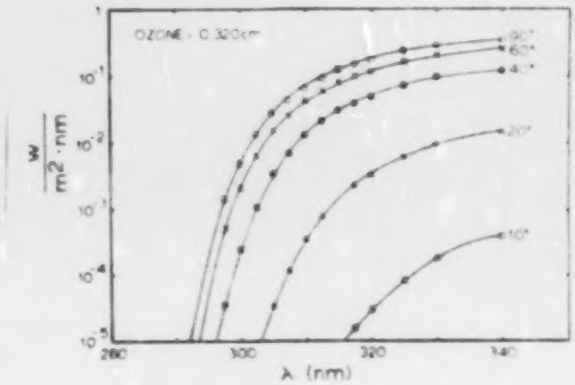


Fig. 4 Solar Direct-Beam ultraviolet energy spectra at several solar elevation angles. Atmospheric ozone content = 0.320 cm STP.

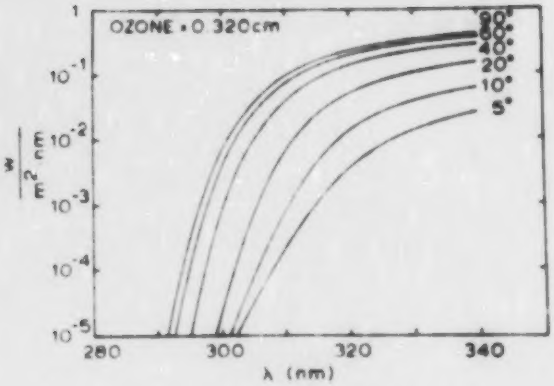


Fig. 5 Diffuse Sky ultraviolet energy spectra at several solar elevation angles. Atmospheric ozone content = 0.320 cm STP.

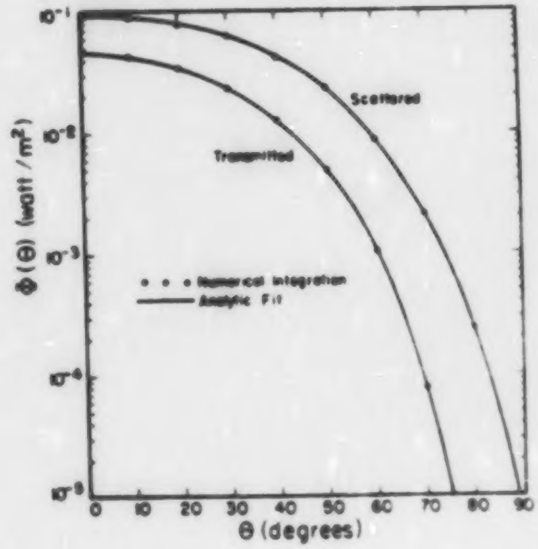


Fig. 7 Transmitted and scattered UV Dose Integrals vs. the zenith angle of the sun, ozone content = 0.320 cm STP.

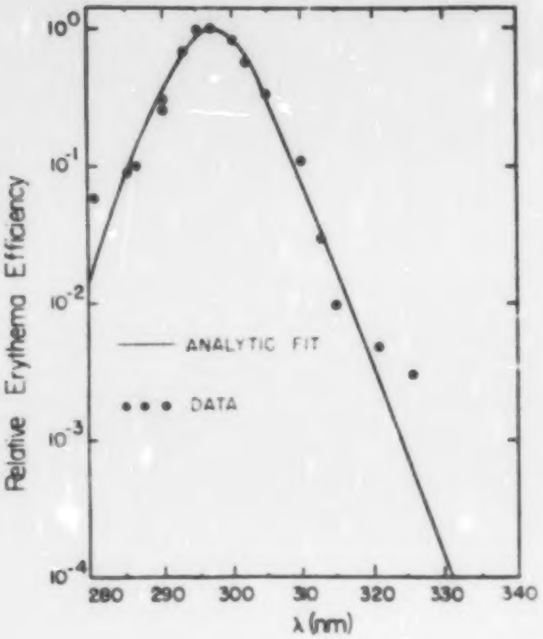


Fig. 6 The spectral efficiency for erythema, data and analytic fit (adapted from GMM).

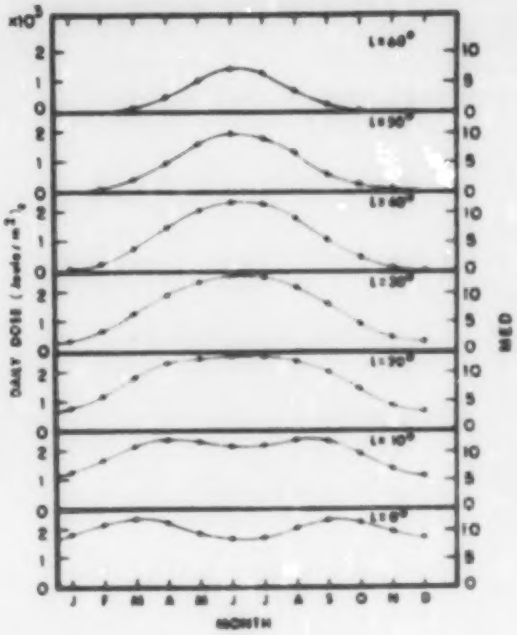


Fig. 8 Daily erythema dose (erythema-spectrum-weighted) under standard atmospheric conditions (ozone content=0.320 cm STP) at various latitudes vs. months of the year (from MG).

Fig. 9 Annual erythema dose as a function of latitude for several percentage ozone reductions from equation (27)

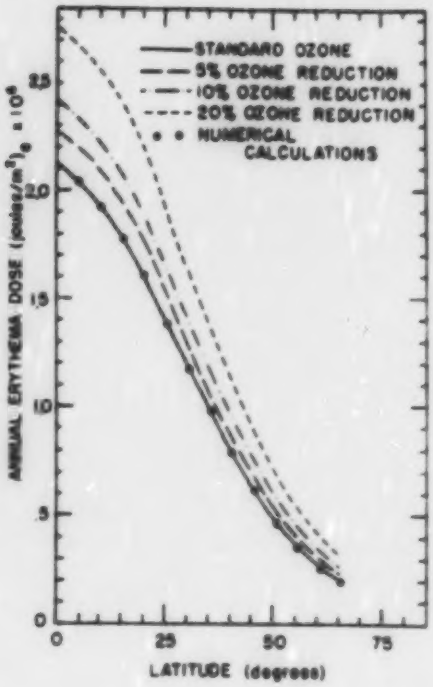
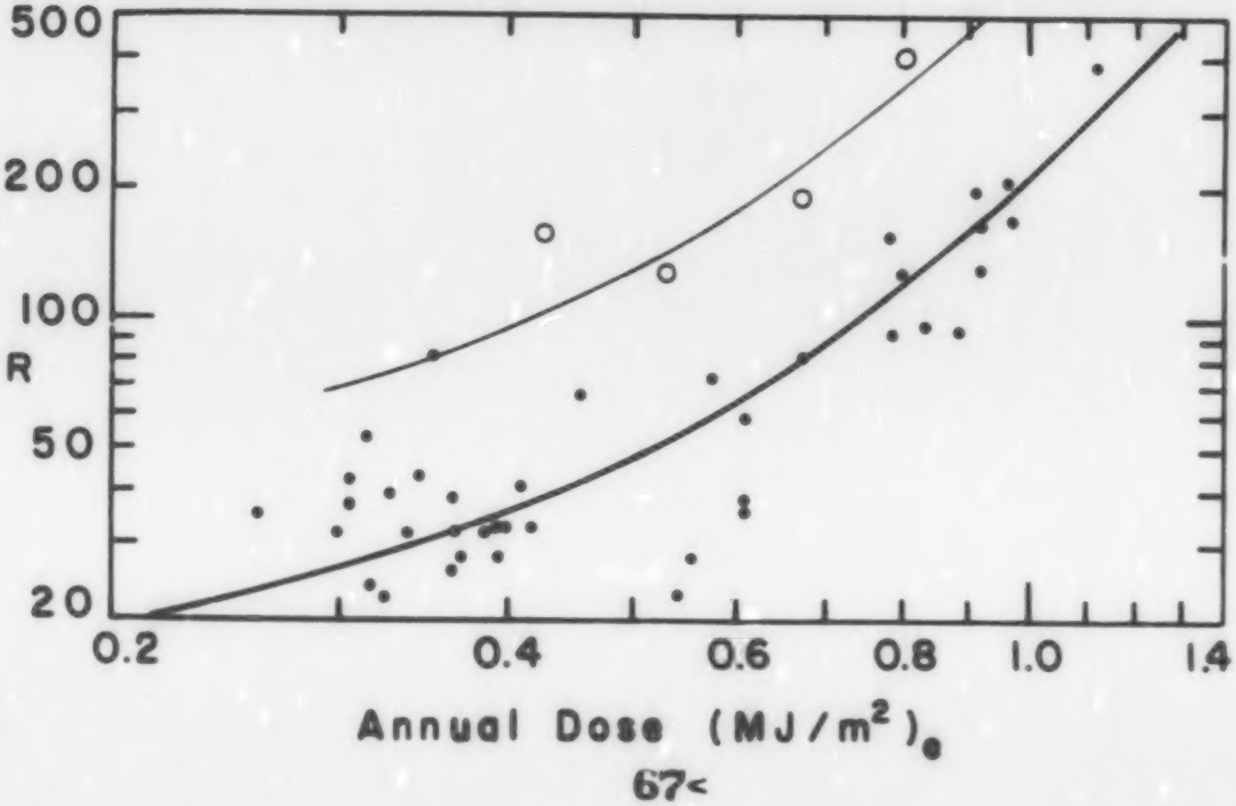


Fig. 10 (below) Age-adjusted non-melanoma skin cancer rate (R) per hundred thousand for the world, (•), and the Third National Cancer Survey (TNCS) (O). The curves are analytic fits with Eq. (30).



ADSORPTION AND TRANSPORT OF POLLUTANTS ON SUSPENDED PARTICLES

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INTRODUCTION

The environmental impact of any pollutant depends largely on its concentration, physical-chemical state and interactions which occur with components of the environment into which it is added. These factors determine the fate and biological effect of all types of pollutants added to air, soil or water. Relationships between the nature of a pollutant and its environmental fate have been documented for transfer and transport processes occurring in water. These will be considered here and an attempt made to identify nonbiological rate-controlling factors determining uptake and transport of common aquatic pollutants.

NATURE OF POLLUTANT

Organic pesticides, hydrocarbons, heavy metals, radionuclides and particulate organic effluents (pulp mill wastes) comprise a partial list of compounds usually considered deleterious in aquatic systems. Unlike other substances, such as inorganic ions (phosphates, nitrates) which readily dissolve, these compounds either emulsify, precipitate, or have a low solubility and remain in colloidal form or adsorb to particulate matter.

Association of pollutants with particulate matter in water greatly alters their subsequent fate. Compounds in solution are only available for uptake by organisms by absorption through membranes. Once precipitated or adsorbed, however, ingestion of concentrated amounts becomes possible. Also, dispersal then follows sedimentation patterns of natural suspended material and the behavior of non-soluble pollutants becomes directly related to the dynamics of naturally occurring particles.

When a compound is added to water, it will either dissolve and enter into true solution, or remain insoluble and form a colloidal or particulate suspension. The initial state which a pollutant assumes determines its subsequent fate (Fig. 1). Compounds of low solubility such as hydrophobic hydrocarbons, may be solubilized to some extent by association with surface active humic-like organic matter (Boehm and Quinn 1973). Such compounds usually form emulsions. Also, if concentrations approach or exceed compound solubility, accumulation occurs at the air-water interface where evaporation occurs. Chlorinated hydrocarbons show this behavior (Oloffs *et al.* 1972) and empirical equations have been derived to calculate potential evaporation rates for hydrocarbons of known vapor pressure and solubility (MacKay and Wolkoff 1973).

Pollutants which do not dissolve, such as wood fiber, become an integral part of the total suspended material and flocculate in a manner similar to naturally occurring suspended particles (Kranck 1974). On the other hand, dissolved metals may be precipitated by changes in electrolyte balance during passage through an estuary (Lowman *et al.* 1966). For example, high molecular weight organic material containing mercury may precipitate at salinity gradients (Lindberg *et al.* 1975). Precipitation and coprecipitation in metallic coatings on particles is also a major mechanism for trace metal transport in rivers (Gibbs 1973).

ADSORPTION-DESORPTION PROCESSES

Pollutants like radionuclides and nutrients which dissolve or like hydrocarbons which form colloidal suspensions have apparent solubilities which are greatly affected by adsorption-desorption reactions with suspended particulate matter. Carritt and Goodgal (1954) review studies which have indicated that suspended solids and colloidal gels can rapidly adsorb nutrients like phosphate. They proposed a mechanism for uptake by rapid adsorption and a slower diffusion controlled reaction. Soluble radiophosphorus and zinc, for example, are rapidly adsorbed by salt marsh sediment (Pomeroy *et al.* 1966). Tritremmel *et al.* (1966) demonstrated that equilibrium concentrations between individual sediment particles and water are reached quickly. Uptake to saturation levels, which varied inversely with particle size, was largely complete within 10 minutes, 50% of maximum values being reached after one minute. Desorption rates were slower. Desorption stabilized after an hour but final equilibrium concentrations were different for different nuclides. Aston and Duursma (1973) have demonstrated similar differences for other isotopes indicating that adsorption depends on properties of both the isotope and the adsorbing surface.

Adsorption-desorption processes also greatly affect the distribution of organic hydrocarbons in water. The hydrophobic nature of many of these substances results in colloidal suspensions and accumulation at interfaces making determinations of true solubilities difficult (Bigger and Riggs 1974). Qualitative and quantitative differences exist in pesticides associated with various size classes of microparticulate matter in natural water (Pfister *et al.* 1969) and it is possible that most hydrophobic compounds are bound to such particles. Cox (1971) points out that most particulate surface area in natural waters is accounted for by suspended matter < 2 μ diameter and it seems likely that hydrophobic compounds will usually be bound to these particles.

Adsorption-desorption processes of pesticides in soil have been extensively reviewed (Bailey and White 1970, Weber 1972). Particle surface area, charge and organic content determine adsorptive capacity in conjunction with water solubility and charge distribution. Huang (1971, 1974) has indicated the extensive adsorptive capacity of clay particles and colloidal humic material for chlorinated hydrocarbons. Pierce (1973) and Pierce *et al.* (1974) also considered the partitioning of *p,p'*-DDT between sea water and suspended particles of various types. Adsorption to suspended clay and sediment occurred by physical adsorption-desorption equilibria whereas adsorption to humic acid occurred by lipophilic binding and capillary adsorption within the humic polymer. Poirrier *et al.* (1972) also noted high adsorptive capacity of colored colloidal material for DDT. Physical rather than chemical adsorption through the formation of weak hydrogen bonds appear to be the primary mechanism for uptake.

Numerous empirical plots can be used to describe adsorbed concentrations as a function of the concentration remaining in solution. Compounds of relatively high solubility (like nitrophenol) may form saturated monolayers, so that uptake becomes asymptotic above certain concentrations. Langmuir isotherms describe uptake of these compounds (Weber and Gould 1966). Adsorption of less soluble compounds, present below saturation levels, however, is usually logarithmically related to concentration, and uptake follows a Freundlich plot

$$X = K\,C^{n} \qquad (1)$$

where X is the amount adsorbed per unit weight of adsorbent, C is the equilibrium concentration in solution, and n and K are constants (slope and intercept) which represent the extent (capacity) and nature of adsorption respectively.

Pierce *et al.* (1974) observed that uptake from dilute concentrations of DDT by various particles was described by Freundlich isotherms with n = 1. Data for uptake experiments described by Hargrave and Phillips (1974) show a similar slope constant. The experiments were repeated using various particles exposed to lindane, aldrin and dieldrin (Fig. 2). The slope constants for Freundlich plots were between 0.80 and 1.70 with a mean value (1.04) similar to published values derived for other compounds (Table 1). This indicates physical binding with absolute values of n determined by the degree of competition of solvent for sites on the adsorbing surface (Khan 1974).

Values of K are an indirect measure of the extent of adsorption. Increased temperature results in decreased values of K indicating the exothermic nature of adsorption which may be proportional to relative free energy changes (Khan 1974). K values are also inversely related to particle diameter by the equation

$$K = a\,d^{-b} \qquad (2)$$

where D is the spherical equivalent of particle diameter (μ) and a and b are constants (Hargrave and Phillips 1974). Haque (1974) attributed high values of K for humic acid to its organic nature, large surface area, and numerous reaction sites. Organic matter in lake sediment and soil is a major determinent for adsorption of non-ionic pesticides (Lotse *et al.* 1968, Wershaw *et al.* 1969). The importance of organic content is further substantiated by a reduction of marine sediment adsorption capacity for DDT by removal of humic material (Pierce *et al.* 1974). Similarly, DDT uptake by sediment of various grain sizes was reduced an order of magnitude after ashing (Hargrave and Phillips 1974).

These observations suggest that a general expression for equilibrium concentrations of hydrophobic compounds on particles of various sizes may be of the form

$$X = \frac{C^{n}}{AD^{b}} \qquad (3)$$

by combining equations (1) and (2). Further expansion to standardize for an effect of organic content on adsorption would be to express uptake per unit organic carbon (or a related index of organic matter) as suggested by Goring (1967) and Hamaker and Thompson (1972). Thus,

$$\frac{X}{c} = \frac{C^n}{a D^b} \qquad (4)$$

Uptake per unit organic matter is directly related to the concentration of a hydrophobic compound in solution and particle surface area available for adsorption. Organic content is often inversely related to particle diameter, however, and thus comparisons of K values and particle size (Hargrave and Phillips 1974) may include effects of this variable. This would explain why over 90% of the variation in uptake by particles ranging in size from bacterial cells to sand grains can be accounted for by only considering differences in median particle diameter and DDT concentration.

Desorption of hydrophobic compounds from particles depends on the nature of the binding, compound solubility, and the length of time available for desorption. For example, DDT adsorbed to humic acid is not desorbed as readily as that on clay or sediment (Pierce *et al.* 1974). Compound solubility is also critical in determining loss rates through desorption. Little DDT is lost from sand on rinsing (Hargrave and Phillips 1974), but lindane and dieldrin are readily lost in proportion to their solubilities (Boucher and Lee 1972). Thus, just as compound solubility determines the concentration available for adsorption to particle surfaces, it also determines desorption rates when concentrations in solution are reduced.

FLOCCULATION PROCESSES

Initially pollutants retain the physical state in which they were introduced and in this state are acted on by physical forces. For example, pollutants associated with coarse-grained sediment dumped from a barge onto mud bottom may never become resuspended for further transport. Fine-grained particulate effluent may disperse widely before flocculating.

Once particles are suspended in a turbulent environment they interact and flocculate with each other and the naturally occurring particles thereby changing their size and hence their transport behavior. The exact mechanism of particle interaction and aggregate formation is poorly understood and only partly predictable at the present time.

Attraction due to molecular forces within the particles and/or adhesion due to organic coatings on surfaces is believed responsible for flocculation. Some mineral species appear to flocculate more readily than others (Whitehouse 1958). Observations with natural suspended particulate matter show that organic matter forms an integral part of flocs. This is not surprising since all surfaces in contact with sea water appear to become coated with organic material. The action of bacteria adhering to particle surfaces may be important in binding flocs. This would diminish the importance of mineralogy in controlling flocculation.

Sediment flocculates in sea water into aggregates the size of which are dependent on the grain size of inorganic particles (Kranck 1975). There is a logarithmic relationship between the modal size of the single deflocculated constituent grains. Flocculation occurs until all particles have approximately the same dynamic transport speed and no longer come into contact with each other. Since particle size and density rather than composition appear to be the controlling factor, the distinct flocculation behavior reported for minerals such as montmorillonite may be a product of their distinct grain size rather than their surface chemistry. Pollutant particles such as organic pulp mill effluent also become incorporated in the natural floc distribution, lose their individual physical characteristics and are transported as part of the natural sediment load (Kranck 1974).

The extent to which suspended particulate matter in fresh water is flocculated is not known. According to classical concepts massive flocculation takes place as unflocculated river sediment comes into contact with saline estuarine water. Some workers, however, have documented the importance of flocculation in lacustrine sedimentation (Sherman 1953). If bacteria are indeed a significant factor in particle flocculation, then flocculation should be as prevalent in fresh water as in the sea.

Microscopic observations of fresh water particulate matter show that a high proportion of the particles consist of aggregates. The grain size spectra show smooth nearly symmetrical distributions similar to those of marine particulate matter (Fig. 3). Since all natural particulate matter contains particles from multiple sources with discrete grain sizes, the size distributions should be irregular multimodal if no interparticle reaction has taken place.

TRANSPORT PROCESSES

Once pollutants become associated with particles their fate is essentially dependent on the transport and dispersal of the particles themselves; they can be sedimented or transported and dispersed. Both can be transitional in that sediment can be eroded and resuspended or sedimented many times.

The transport and dispersal of particles is dependent on the transport rate of the water and on the relationship of the transport rate of particles to that of the water. Dissolved pollutants can be expected to disperse at the same rate as the parcel of water into which they were introduced. But particles usually have specific gravities greater than that of the water and gravity and inertia will give them a slower net motion. Only very small particles and particles with densities close to that of water will behave as dissolved substances. Progressively larger and heavier particles will have transport histories increasingly different from that of the water they are suspended in, and particle size and density are of primary importance in prediction of their transport behavior.

Models to predict transport rate of suspended sediment in relation to dynamic water transport are presently imperfect. The movement of large sand and silt particles transported as bedload with a rapid exponential decrease in concentrations away from the bottom is best understood. Their behavior has been studied in numerous laboratory and theoretical investigations (Sternberg 1967, Sundborg 1956). The fine-grained suspended load, composed mostly of cohesive material less than 16 microns, shows physical behavior different from that of the bedload and are easily distinguished from the bedload in grain size analysis of bottom sediments (Visher 1969). Suspension of the material is largely dependent on levels of microturbulence and the highest concentrations are often encountered near the surface and near the bottom of a water body as well as in association with density layers within the water column (Heathershaw and Simpson 1974, Drake and Gorsline 1973).

At present the best guide to where particles of a given size will be deposited seems to be an empirical study of geological conditions along an aquatic pathway. For example, whether or not a pollutant associated with particles of a certain size can become deposited in a lake along a waterway or trapped in the turbidity maximum of an estuary may be determined by comparison of natural sediment grain size and that of the polluted material.

SUMMARY

In conclusion it can be shown that pollutants entering the aquatic environment readily become associated with natural suspended particles. Dissolved compounds are adsorbed onto particles and substances in particulate form flocculate with other particles. The division between true solutions and colloidal suspension may be difficult to determine and is of no practical significance if both forms ultimately become associated with other particles.

Particle size and concentration are of prime importance in predicting transport and dispersal of pollutants. While the organic nature and surface charge of suspended particles affect adsorption, particle size and number (i.e. total surface area) may be the most important factor determining adsorption of non-soluble pollutants in water. Transport of particles after adsorption and flocculation is dependent on the relationship between grain size and the turbulence of the hydraulic environment.

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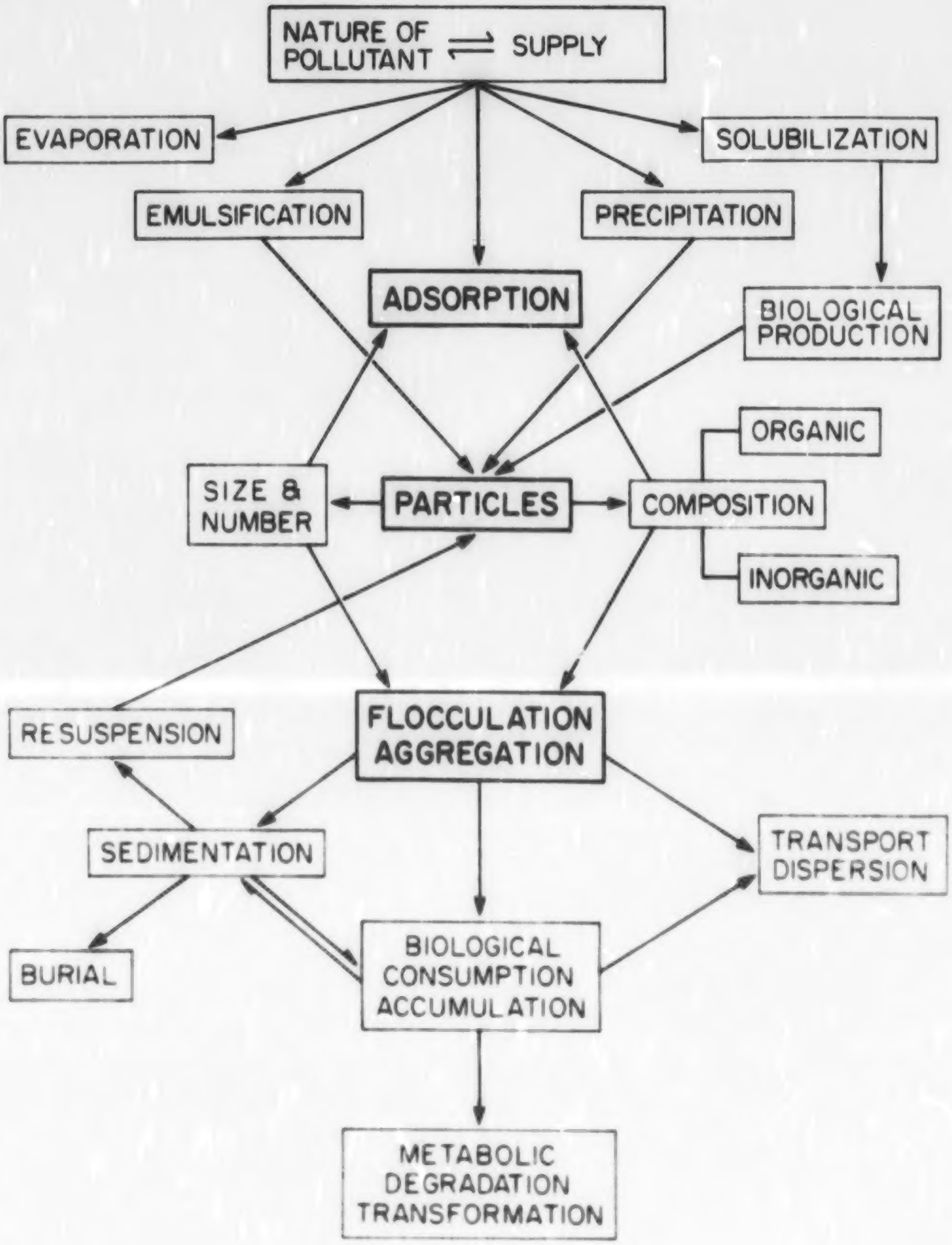
Table 1 - Comparison of Freundlich adsorption constants (n = slope, K = intercept) for uptake of different compounds by particles of various size and type.

Compound	Surface	Temperature (C)	n	K	Reference
Lindane	lake sediment	23	0.92	0.30	Lotse et al(1968)
Arochlor 1254	illite clay	26	1.10	63	Haque et al(1974
	soil		0.81	26	
2,4-D	fulvic acid-clay	5	0.76	6.6	Khan (1974)
		25	0.83	5 2	
	illite	0	0.69	12.9	
		25	0.72	10.5	
	montmorillonite	0	0.93	0.87	
		25	1.00	0.65	
	sand	0	0.67	0.11	
		25	0.83	0.04	
2,4-D	alumina	0	0.97	0.87	Haque (1974)
		25	1.01	0.83	
	silic gel	0	0.90	3.8	
		25	0.95	1.3	
	humic acid	0	0.86	102.3	
		25	0.93	79.4	
	humic acid	25	1.00	245	
-DDT	marine sediment	25	1.00	48	Pierce et al (1974)
	kaolinite clay	25	1.00	6	
P,P'-DDT	2µ silt	10	1.15	320	Hargrave and Phillips (1974)
	12µ silt	10	1.68	86	
	46µ sand	10	1.02	8	
	270µ sand	10	0.86	0.32	
	605µ sand	10	0.83	0.07	
	1500µ sand	10	0.80	0.02	
	250µ sand (ashed)	10	1.16	0.02	
Aldrin	2µ silt	10	1.24	242	Hargrave (unpublished)
	20µ pollen grains	10	1.17	604	
	90µ sand	10	1.10	1.5	
	294µ sand	10	0.93	0.20	
	855µ sand	10	0.80	0.04	
Lindane	10µ silt	10	1.05	37.2	Hargrave (unpublished)
	428µ sand	10	0.94	0.003	
Dieldrin	10µ silt	10	1.11	405	Hargrave (unpublished)
	428µ sand	10	0.92	0.04	
	855µ sand	10	0.86	0.006	



ADSORPTION AND TRANSPORT PROCESSES OF POLLUTANTS ON SUSPENDED PARTICLES

NATURE OF POLLUTANT ⇌ SUPPLY
EVAPORATION
SOLUBILIZATION
EMULSIFICATION
PRECIPITATION
ADSORPTION
BIOLOGICAL PRODUCTION
ORGANIC
SIZE & NUMBER
PARTICLES
COMPOSITION
INORGANIC
FLOCCULATION AGGREGATION
RESUSPENSION
SEDIMENTATION
TRANSPORT DISPERSION
BURIAL
BIOLOGICAL CONSUMPTION ACCUMULATION
METABOLIC DEGRADATION TRANSFORMATION

Figure 1. Schematic outline of major processes which affect adsorption and transport of nonsoluble pollutants in water.

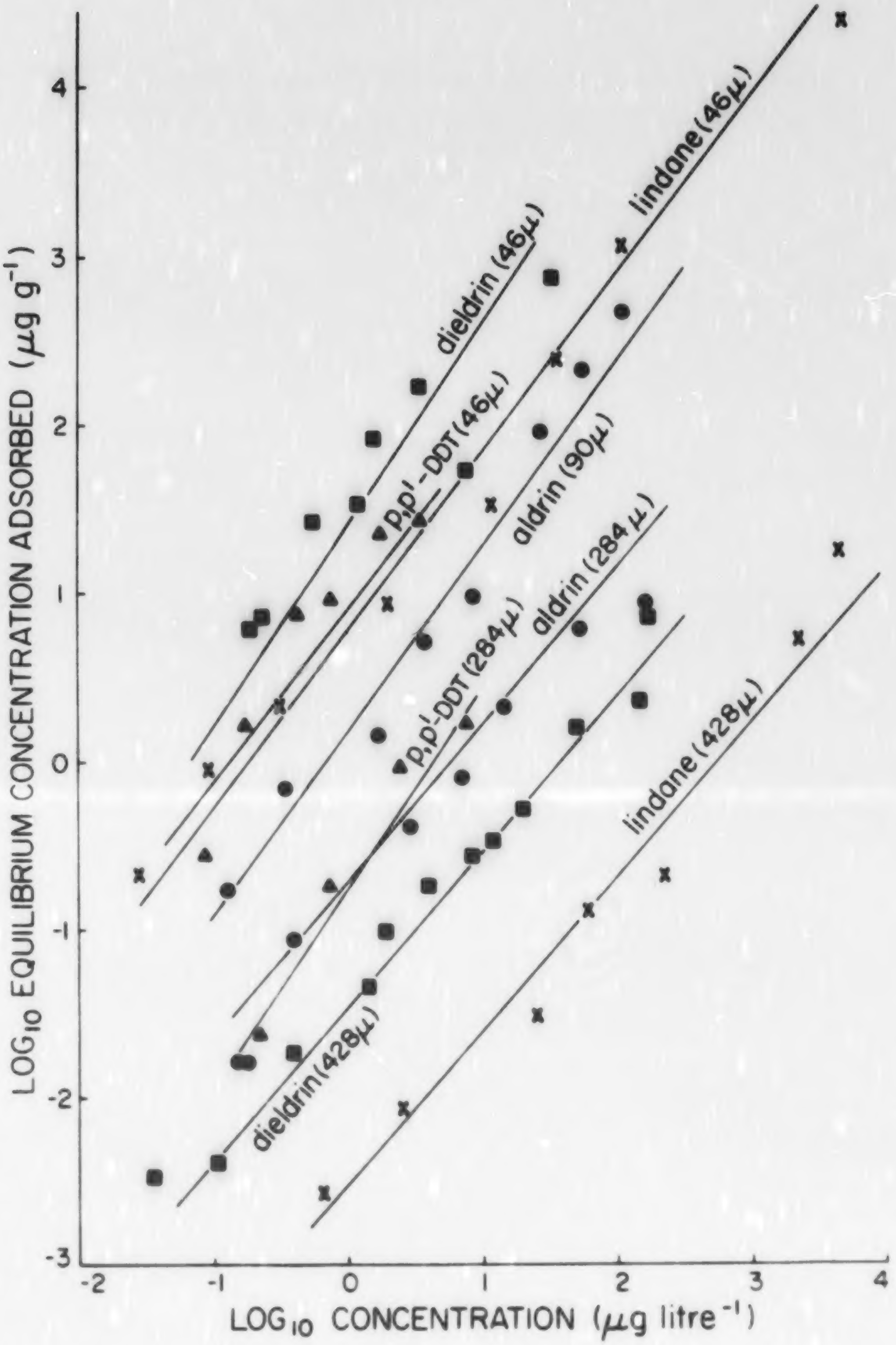


Figure 2. Freundlich isotherm diagrams for p,p'-DDT, lindane, aldrin and dieldrin on sand particles of various sizes. Adsorption measured after equilibrium concentrations on particle surfaces were reached (24-36 hr). No correction for desorption was applied to the data.

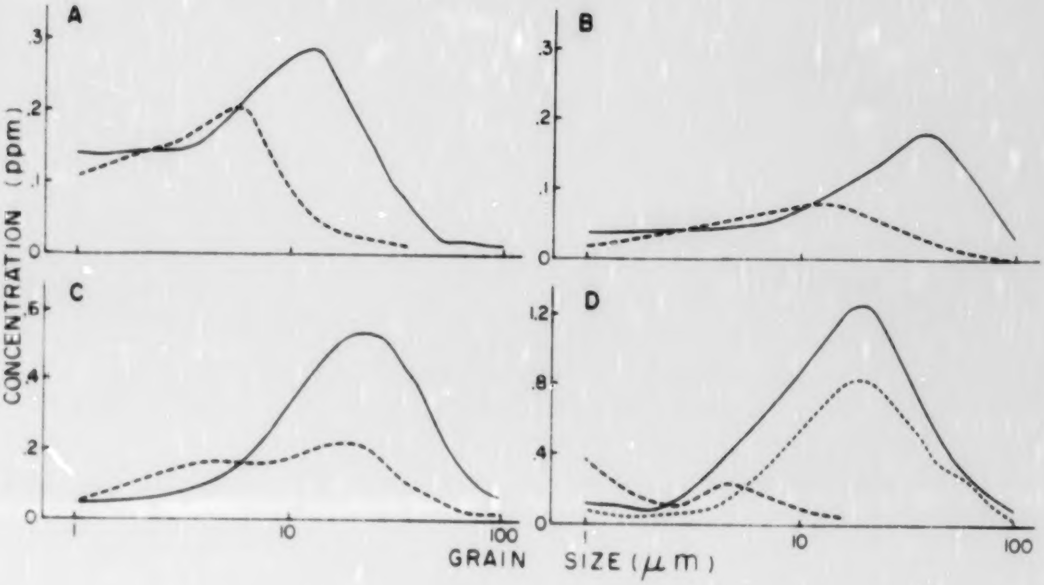


Figure 3. A to C. Suspended particulate matter grain size spectra illustrating smooth unimodal distributions typical for natural material. Solid line shows natural distribution and dashed line shows distribution of deflocculated inorganic grains. A: Fresh water, Lake of Two Mountains, Que. B: Fresh water, Miramichi River, N.B. C: Sea water, Petpeswick Inlet, N.S.

D. Effluent particles artificially flocculated with natural sediment distribution to produce smootn unimodal distribution. Dashed line shows effluent particles, short dashed line shows natural sediment distribution. Solid line shows total distribution resulting from 15 hours of gentle agitation.

PHOTOLYSIS OF PESTICIDES ON SOIL SURFACES(1)

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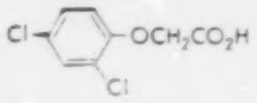
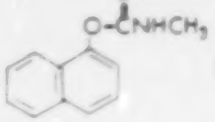
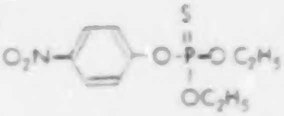
Introduction

The role of photochemical decomposition in the degradation of pesticides on soil surfaces is at best very nebulous. A number of studies indicate that pesticide photochemistry is quite sensitive to the precise nature of the surface and that studies using silica or glass as soil models may be very misleading.[2,3] The analytical problems encountered in monitoring this aspect of decomposition in the "field" are great and any definitive conclusions are lacking.(2) As a result it is necessary to approach the problem with controlled laboratory studies by simulating selected variables expected under environmental conditions. We have examined the photochemical decomposition of 2,4-D (I), Sevin (II) and Parathion (III) on three types of arable soils. Our interest was in determining the extent to which surfactant additives (simulating pesticidal formulations) may influence the photochemistry. The moisture content of the soils has proved to be a critical variable.


I


II


III

Experimental Conditions

The soils used in our studies are typical arable types differing widely in pH, organic content, nature of exchangeable cations present, etc. Pertinent characteristics are given in Table I. The surfactants studied were of the anionic (sodium dodecyl sulfate, SDS) and cationic (hexadecyltrimethylammonium bromide, HDTBr) types. The moisture content of the soils was varied and can be categorized as follows:

Table I. Soil Characteristics

Type	Name	Slurry pH	%Carbon	Bulk Density	% Pore Space
I	Etowah	4.4	0.13	1.70	35.8
II	Holston	6.3	0.60	1.90	28.3
III	Conasauga Siltloam	7.6	2.79	1.57	40.8

(1) Dry: soil which has been dried with no additional water added.

(2) Saturated: dried soil to which a quantity of water has been added to fill the "pore space". This quantity depends on the individual soil and amounts to roughly 1 ml. per gram soil. It has been found that when detergents are co-applied an additional quantity of water is required to give the visual appearance of saturation. The additional quantity is probably used in hydration of the surfactant head group.

(3) Wet-quantites of water (up to 4 ml) are added to saturated soils to form slurries.

The general procedure involves preparation of a uniform soil surface by spreading an aqueous slurry containing one gram soil on a 10x15 cm surface (Figure 1) and allowing the surface to dry completely. The pesticide (5 mg) and, in certain cases, detergent (100 mg) are dissolved in 5 ml acetone or methanol and spread uniformly on the thin soil film. The solvents are evaporated completely. This corresponds to a coverage of 2.9 lbs. pesticide per acre and 58 lbs surfactant per acre. For those experiments involving water saturated or wet soils, an appropriate amount of water is uniformly added to surface. The vessel is then sealed and photolyzed (Figure 1). An identical vessel is simultaneously prepared and stored in the dark for an equivalent time period.

The samples are photolyzed on custom built glass tray with cooling water circulating on the under side to avoid evaporative losses and to maintain the initial moisture content. The trays are tightly covered with Pyrex glass on top and are placed about 6 inches under a horizontal water-cooled Pyrex-jacketted medium pressure Hg arc (450 w). The radiant density is reasonably uniform over the entire surface.

After photolysis the soil films are exhaustively extracted and the extract is prepared for analysis by gas chromatography (2,4-D and Parathion) or high pressure liquid chromatography (Sevin). In the case of 2,4-D the extract is treated with BF_3-CH_3OH to esterify the carboxylic acids. Appropriate controls have indicated that the procedures employed allow near quantitative recovery of the pesticides and expected decomposition products.

The output of the lamp as constructed and filtered by Pyrex provides radiation with approximately the following photon flux on the plate surface.

λ (nm)	total incident light (Einsteins-sec^{-1})
297	0.58×10^{-7}
303	1.4×10^{-7}
313	4.4×10^{-7}
314	1.1×10^{-7}

Longer wavelength light is not absorbed by the pesticides used and shorter wavelength light is totally filtered by the Pyrex. For Sevin and 2,4 D the quantity applied is such that only a small fraction of the incident intensity is absorbed. Consequently, it is expected that the extent of photolysis should fall off exponentially with time. Experiments at various time intervals have confirmed this expectation. The bulk of our experiments have been run at exposure times of 18-150 hrs, but in order to facilitate comparison the results have been calculated and are reported in terms of the time required for 50% photodecomposition.

Very crude quantum yields can be calculated by assuming that extinction data in solution is applicable to soil surfaces.

Results

The photolysis of 2,4-D was carried out on the acid rather than the various esters actually used as pesticides because it was found that hydrolysis of the ester to the acid occurred very rapidly on the soils studied. Representative results are given in Table 2.

Several factors are apparent from these results. The dry and water saturated soils behave similarly. The anionic surfactant decreases the extent of photolysis on dry or saturated soils. In the presence of either detergent excess water dramatically increases the rate of photolysis. In the absence

Table 2. Effects of soil types, detergents and soil water content on the time required for 50% photodecomposition of 2,4-D.

Soil	Detergent	Water Content	Time required for 50% Photodecomposition
I	none	wet	144 hr
I	HDTBr	wet	49
I	SDS	wet	19
I	HDTBr	satd.	55
I	SDS	satd.	175
I	SDS	dry	145
II	none	wet	149
II	HDTBr	wet	35
II	SDS	wet	< 14
II	HDTBr	satd.	64
III	none	wet	440
III	HDTBr	wet	<4
III	SDS	wet	<10
III	HDTBr	satd.	55
III	SDS	satd.	139
III	none	dry	58 ($\phi \sim 0.004$)
III	SDS	dry	175

of detergent excess water actually decreases the rate of photolysis. For purposes of comparison to solution photodecomposition a crude quantum yield of 0.004 can be estimated for the experiment designated in Table 2. In aqueous solution the quantum efficiency for photodecomposition of 2,4-D is approximately 0.1.

Studies using the pesticide Sevin were carried out only on dry and water saturated soils. Problems with hydrolysis to a -naphthol precluded studies with wet slurries. Representative results for this system are presented in Table 3. Note that in three cases decomposition in the dark was the most significant process. In all other cases, decomposition in the absence of light did not interfere to any significant extent. These analyses were done on samples exposed for 72 hours. However the results are reported in the same manner as those for 2,4-D in order to facilitate comparison. In general the photolysis of Sevin on soils is very inefficient. A crude approximation of the quantum yield for the most favorable case in Table 3 is ca. 0.0004. In solution the quantum yields are approximately 0.01 to 0.03.

Table 3. Effects of soil types, detergents and soil water content on the time required for 50% photodecomposition of Sevin.

Soil	Detergent	Water Content	Time required for 50% Photodecomposition
I	none	dry	97 hr
I	none	satd.	long (no loss in 72 hr)
I	HDTBr	dry	251
I	HDTBr	satd.	274
I	SDS	dry	274
I	SDS	satd.	251
II	none	dry	251
II	none	satd.	1700
II	HDTBr	dry	440
II	HDTBr	satd.	(a)
II	SDS	dry	251
II	SDS	satd.	251
III	none	dry	105
III	none	satd.	(b)
III	HDTBr	dry	381
III	HDTBr	satd.	72 (c)
III	SDS	dry	251
III	SDS	satd.	440

(a) about 22% is decomposed under either the dark or photolytic conditions in 72 hr.
(b) about 17% is decomposed under either the dark or photolytic conditions in 72 hr.
(c) in the dark control 36% is decomposed to give an unknown material, 31% appears as a -naphthol and 32% Sevin remains; in the photolysis only 30% Sevin remains in 72 hr.

Our studies with the pesticide Parathion are in preliminary stages. Representative data for photolysis on Soil III are given in Table 4.

Table 4 Effects of detergents and soil water content on the time required for 50% photodecomposition of Parathion on Soil III.

Detergent	Water content	Time required for 50% Photodecomposition
none	dry	150 hr
none	satd.	60
HDTBr	dry	173
HDTBr	satd.	159
SDS	dry	254
SDS	satd	83

Analysis of the extracts revealed no p-nitrophenol or paraoxon. Controls showed that 100% of either could be recovered from the soil with the workup procedure employed. Studies are currently in progress to determine how rapidly either would photodecompose under the photolysis conditions.

Conclusions

It is clear each of the factors (soil type, detergents, moisture content) studied exerts a different effect on each pesticide. Mechanistic explanations for these effects are currently being pursued. Photolysis on these soils occurs at a much slower rate than in solution.

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1. Address: Department of Chemistry, University of Georgia, Athens, GA. 30602; the experimental work was carried out by Dr. Ram D. Laura; Financial support from the United States Environmental Protection Agency (grant R-802959) is gratefully acknowledged.

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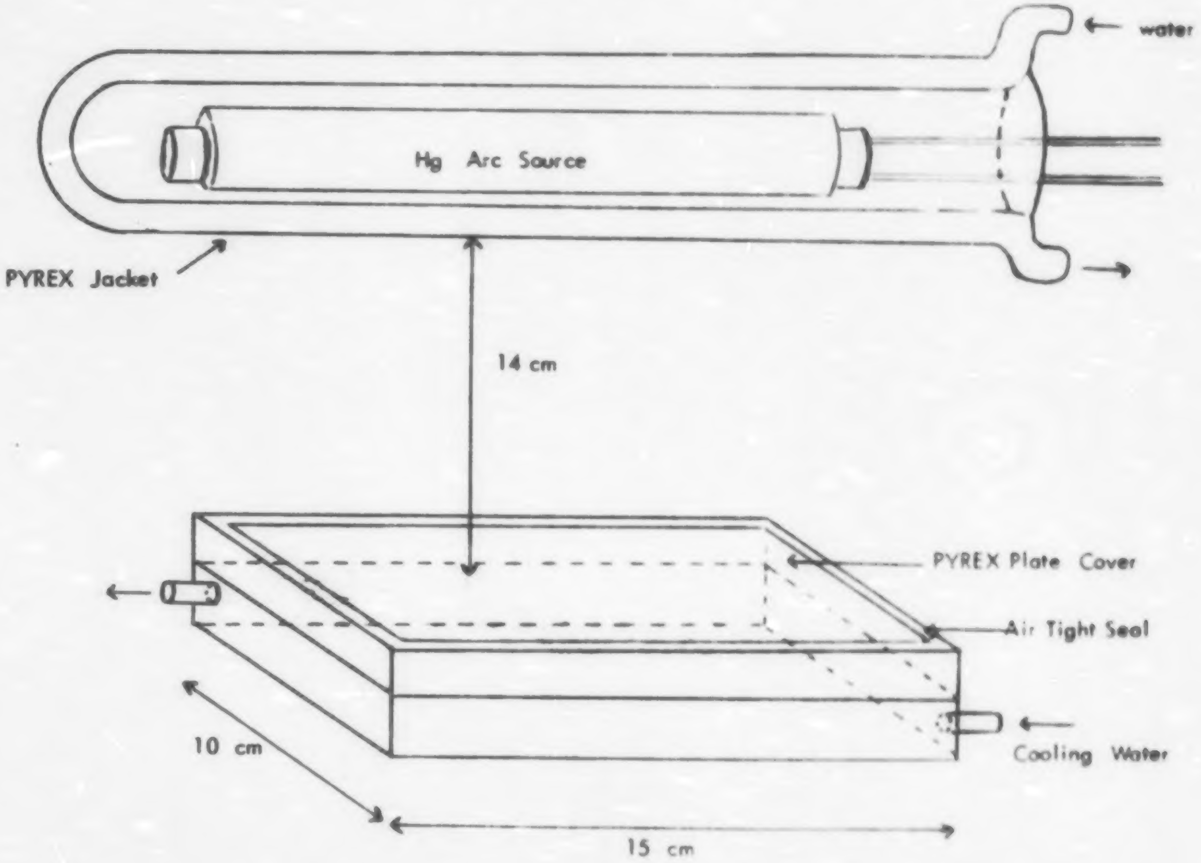
3. J.R.Plimmer in "Fate of Pesticides in the Environment", Proceedings of the Second International IUPAC Congress of Pesticide Chemistry, Vol. VI, ed. by A.S.Tahori, Gordon and Breach Pub., New York, 1972, pp. 47-76.

Figure 1. APPARATUS FOR PHOTOLYSIS ON SOIL SURFACES


← water
Hg Arc Source
PYREX Jacket
14 cm
PYREX Plate Cover
Air Tight Seal
Cooling Water
10 cm
15 cm

Predictive Modeling of the Behavior of Pollutants in the Aquatic Environment

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Introduction

Predictive models differ mainly in their scope and applicability. Models used to predict chemical and physical phenomena for controlled laboratory conditions are at one extreme of predictive scope and applicability. At the other extreme are models used to predict future events and conditions of some natural system, e.g., models of weather, hydrology, or water quality. Between these extremes, models can be used to classify the behavior and fate of substances with respect to specified environmental conditions and to evaluate factors and processes important in their behavior and fate. Models intended for these purposes can be called evaluative models. A model for mercury was chosen to illustrate some of the problems of construction, conceptual difficulties, and data needs for evaluative models.

Evaluative models are usefully applied wherever detailed relationships can be described mathematically, but where the overall complexity is too great for net results to be clear. Much is known of the chemistry and physics of mercury, yet the factors influencing its behavior are too complex for its fate in a given environment to be apparent. Therefore, it is a useful subject to illustrate the concepts of an evaluative model.

The mathematical model used was structured to explore the possibility of predicting the fate of mercuric ion and its complexes (Hg_T), ionic methyl mercuric species (CH_3HgX_T), and elemental mercury (Hg^0) in aquatic systems. A schematic representation of the major features of the system is given in Figure 1. The aquatic system that is represented consists of a body of moving water in contact with the atmosphere and the underlying sediments.

Model Description

A set of differential equations is used to represent the forms of mercury in the system. Each equation is similar to the following:

$$\frac{\partial\,[Hg]}{\partial t} = \frac{D\,\partial^2[Hg]}{\partial x^2} - \frac{V\,\partial[Hg]}{\partial x} + S([Hg])$$

in which the first term on the right represents dispersion, the second advection, and the third the algebraic sum of the sources and sinks relating to this form of mercury. The source-sink terms, S, are written as functions of environmental descriptors, e.g., pH, concentration of suspended particulate material, or depth of sediment and water. Although a great deal is known about the chemistry of mercury, none of the source or sink terms can be written without conjecture. Nevertheless, an attempt was made to structure each term to reflect as much as is understood about the chemistry of the process.

An example from the mercury model will illustrate some of the uncertainties accompanying the writing of source or sink terms. Oxidation and reduction of elemental mercury and mercuric ion, respectively, is described by the following equilibrium expression (Parks, G.A., pers. comm.)

$$K_{red}^{ox} = \frac{[Hg^0]\,[H^+]^2\,PO_2^{1/2}}{[Hg^{2+}]} = 10^{-\text{[illegible]}}$$

However, observations from several types of experiments show that the reactions do not proceed rapidly to completion, i.e., solutions containing mercuric ion continue to produce elemental mercury for days (1,2,3). Because of these observations the reactions are better represented by rate terms rather than by algebraic equilibrium expressions. Equilibrium expressions do not necessarily reflect mechanisms, and rate expressions cannot properly be obtained from them. In spite of this fact, the following reactions, given by Parks (4), were used to represent oxidation and reduction pathways:

$$Hg^{2+} + H_2O \underset{k_o}{\overset{k_r}{\rightleftharpoons}} Hg^0 + 2H^+ + \tfrac{1}{2}O_2$$

The rate expression for oxidation was taken to be

$$k_o\,[Hg^0]\,[H^+]^2\,[O_2]^{1/2}$$

The rate expression for reduction was

$$k_r\ [Hg^{2+}].$$

For the environment reduction cannot be as simply represented as this term. It is complicated in most natural waters by the presence of suspended particulate material which is probably encased by a layer of organic material (5). Mercuric ion complexes strongly (6) with sulfhydryl-containing compounds and will therefore be expected to bind strongly to suspended particulates. The question facing the modeler is whether reduction of mercuric ion bound to particulates can be represented by a simple proportion as assumed for dissolved. If not, the bound mercuric ion concentration must be computed. The following equations are used as an approximation for computing the bound mercuric ion, also taking into account hydrolysis.

$$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+$$

$$HgOH^+ + H_2O \rightleftharpoons Hg(OH)_2 + H^+$$

$$Hg^{2+} + \mathcal{P} \rightleftharpoons Hg\mathcal{P} + 2H^+$$

Here, $\wp$, is a symbol for suspended particles treated as though they are a dissolved constituent. The three equilibria are

$$\frac{[HgOH^+]\quad[H^+]}{[Hg^{2+}]} = K_1$$

$$\frac{[Hg(OH_2)]\ [H^+]}{[HgOH^+]} = K_2$$

$$\frac{[Hg\wp]\ [H^+]^2}{[Hg^{2+}]\ [\wp]} = K_p$$

Assuming that $[Hg^{2+}] << [\wp]$ and is so low that the reactions do not affect $[H^+]$, there are four unknowns $[Hg^{2+}]$, $[HgOH^+]$, $[Hg(OH)_2]$, $[Hg\wp]$. A mass balance equation for Hg_T provides the other information necessary for solution:

$$[Hg_T^{2+}] = [Hg^{2+}] + [HgOH^+] + [Hg(OH)_2] + [Hg\wp].$$

The bound fraction, β, is

$$\beta = \frac{K_p[\wp]}{[H^+]^2 + K_1\ [H^+] + K_2K_1 + K_p[\wp]}$$

and the free mercuric ion fraction, δ, is

$$\delta = \left[1 + \frac{K_1}{[H^+]} + \frac{K_2K_1 + K_p\ [\wp]}{[H^+]^2}\right]^{-1}$$

Depending upon whether reduction of only free mercuric ion or of both bound and free can be described by the constant proportion, the reduction term is either

$$k_r\ \delta\ [Hg_T^{2+}]$$

or

$$k_r\ (\beta + \delta)\ [Hg_T^{2+}].$$

Each term in the model was subject to similar uncertainties. The question of how to express accepted chemical, biochemical or other equations in the context of a complex natural system is the basic difficulty facing the "environmental modeler".

Some of these questions might be theoretically answerable, but most will be solved only through observation and experiment. For the example above, results may be obtained by testing each case, reduction of bound mercury and

reduction of both bound and soluble. If the results are different, that difference may be used to design a critical experiment to detect which hypothesis, if either, is correct.

Results and Discussion

Two kinds of quantities were checked for their importance to the environmental behavior of mercury. One kind is solely a property of the environment, e.g., pH, suspended sediment load. The other is best considered as an interaction of mercury and the environment, e.g., volatilization rate, strength of binding to particulates. Their importance was judged on the basis of the sensitivity of the forms of mercury to variation in these quantities. Several computations were made before arriving at a set of initial values that is reasonably compatible with the rates and equilibria assumed for the system. The initial values selected are

for water:

Mercuric	2×10^{-12}M
Methyl	2×10^{-16}M
Elemental	8.5×10^{-12}M

and for sediment:

Mercuric	2.2×10^{-9}M
Methyl	2.6×10^{-14}M
Elemental	2×10^{-11}M

These values are not defensible as being "realistic", nevertheless, they are useful in two ways. First, they provide a starting point from which further computations can be made. Second, discrepancies from expected values may point to deficiencies in the current representation.

Physically, one kilometer of a very slowly moving body of water is represented. Each data point is taken after a 20-day simulation and the sampling point chosen is that of the lower end of the one-kilometer reach. This procedure was adopted so that the points would indicate conditions at a distance from a low level source.

It has been speculated that solids in aquatic systems control the fate of mercury. In assessing this possibility, the equilibrium constant, K_p, for binding of mercuric ion to sediment was varied over five orders of magnitude, while the concentration of suspended particulates was held constant at 10 mg/l. A marked dependence of all forms of mercury on K_p is apparent. Methyl mercury concentration is much higher in the sediments for low values of K_p (Figure 2). The opposite is noticed in the water (Figure 3). These observations result mostly from the model assumptions that both the methylation and reduction processes occur for bound mercuric mercury, and that there is no settling of suspended particulates.

An alternative way to evaluate the importance of suspended particulates in the system is to vary the particulate load itself. In this analysis K_p was held constant at 1.5×10^{-2} (equivalent to a partition coefficient of 1.5×10^{12} at pH 7) and suspended sediment was varied over a range of five orders of magnitude (Figures 4-6). Elemental (Figure 4) and mercuric mercury in the sediments decrease as expected with increasing suspended sediment load. Surprisingly, however, methyl increases in the sediment (Figure 5). In the model methyl mercury is formed microbially from mercuric mercury that is bound to particulate material. A greater suspended particulate load results in greater production of methyl mercury. The greater quantity of methyl mercury in sediments results from the greater production rate and resulting greater concentration (Figure 6) in the water, followed by sediment water exchange and binding of methyl mercury to the sediment particles.

At $K_p = 1.5 \times 10^{-2}$ and 10 mg/l of suspended particulates, all forms were remarkably insensitive to changes in pH. Preliminary computations indicate, however, that a major change in the concentration of all forms occurs between pH4 and 5.

Certain aspects of the physical geometry of the system could result in variation in the concentrations of the mercury forms. For this simple model only depths of water and sediment may be varied. The depths of water and sediment were each varied three orders of magnitude. Mercuric mercury concentration in the water was completely insensitive to sediment depth, but was a rather strong function of water depth. Elemental mercury in the water (Figure 7) was positively correlated with variation of both water and sediment depth but was more strongly a function of water depth. Elemental mercury in a sediment, however, was affected markedly by sediment depth (Figure 8) and nearly unaffected by water depth, especially for the situations with deeper sediments.

Conclusions

As a result of both constructing and using an evaluative model for mercury, two deficiencies can be identified. The uncertainty about the way that the transformation processes operate is the most basic deficiency. The processes cannot be described mathematically and used in a model unless they are understood. Second, uncertainty about the value of such parameters as the equilibrium coefficient for binding of forms to particulate materials, limits the confidence that can be placed in results obtained from the model.

The behavior of a substance in the environment is assumed to result solely from the interaction of certain quantities considered to be properties of the substance and others considered properties of the environment. Many of the properties of elements have been studied, catalogued, and are widely available. Some quantities such as a partition coefficient of mercuric mercury between particulate material and water are, by nature of the measurement, quantities that chemists naturally would measure. Unfortunately, by nature of the material, these quantities are more likely to be considered properties of the environment. Chemists usually prefer to work with defined chemicals rather than "particulate material", and therefore measurements of this sort often are not made.

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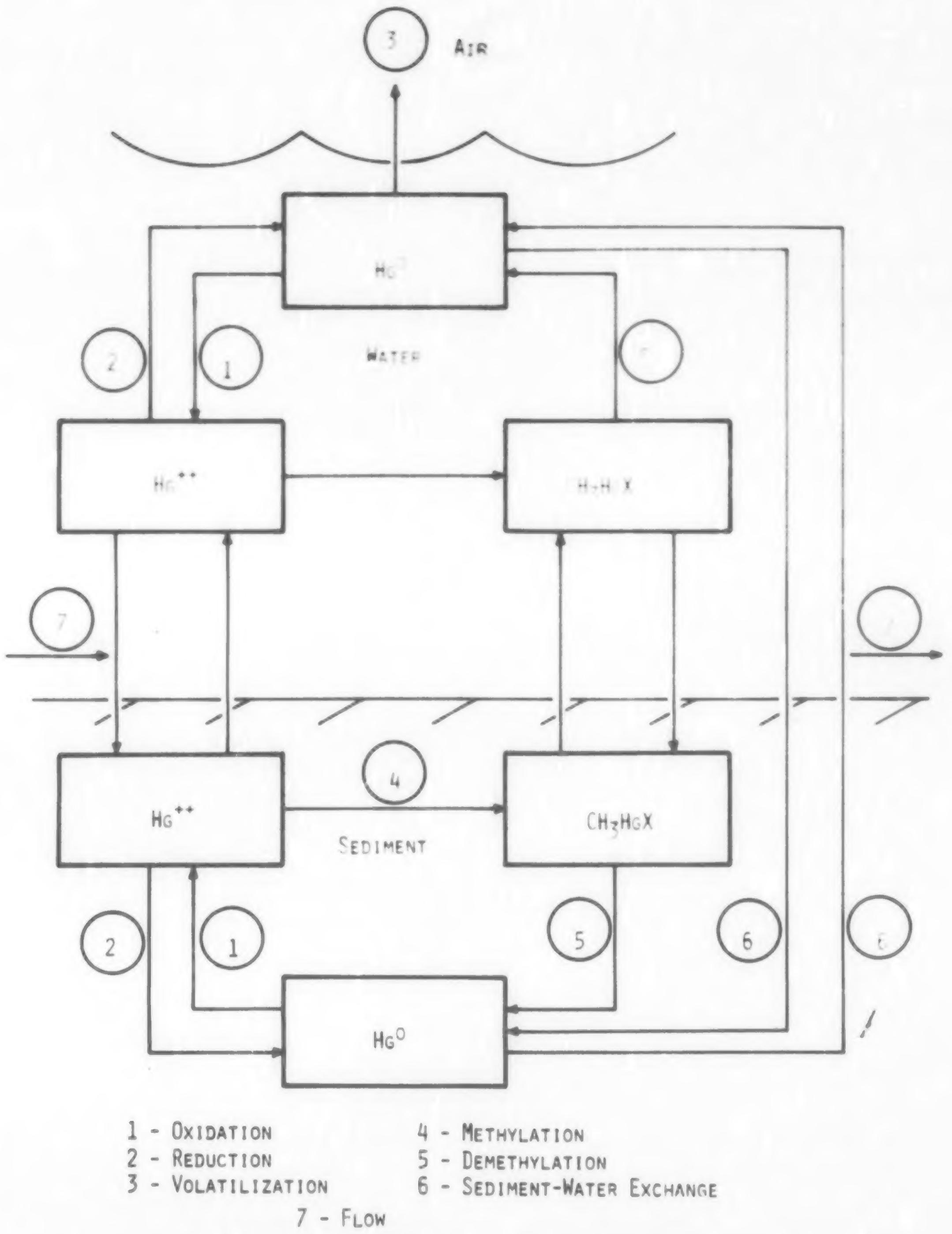
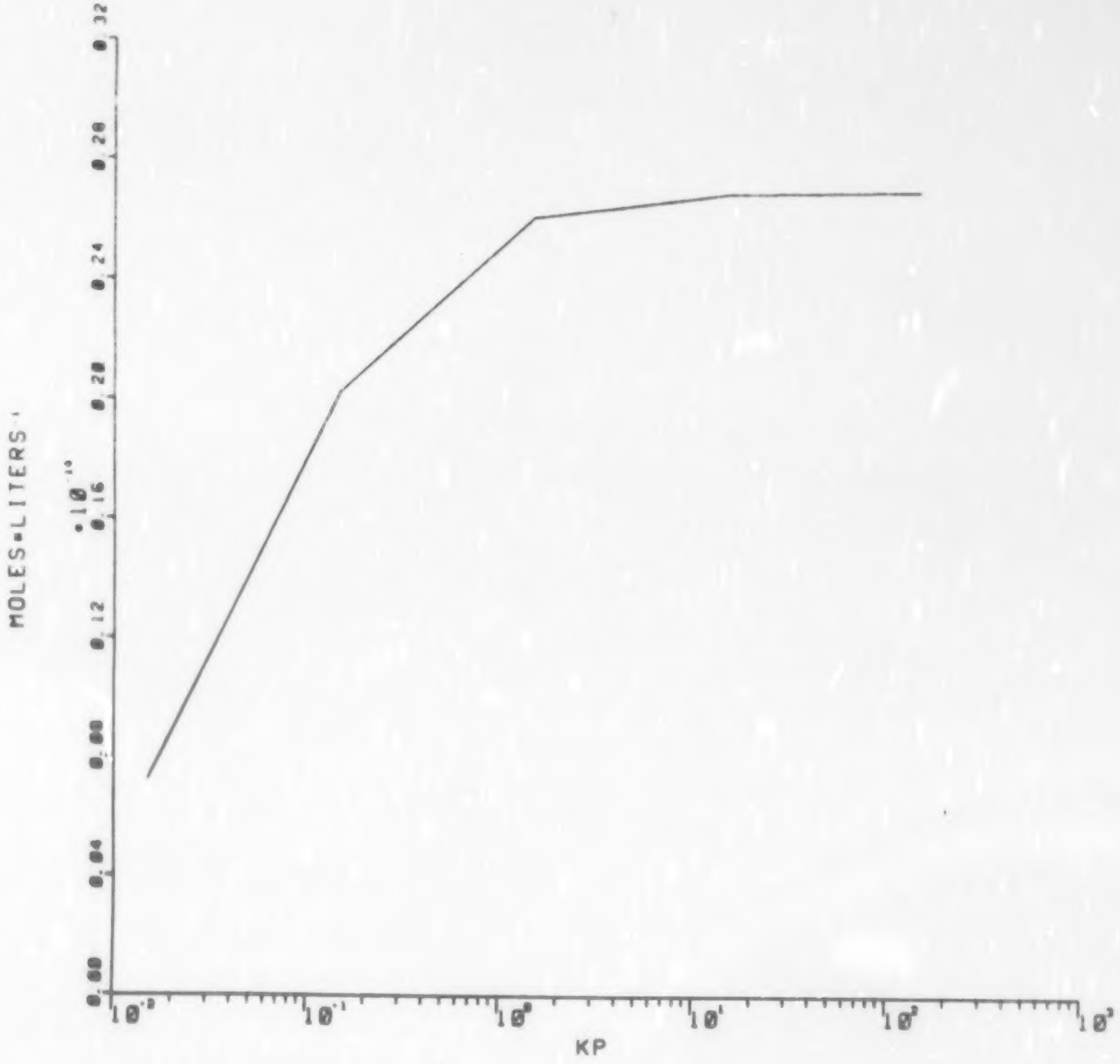
Figure 1


3
Air
Hg^0
Water
2
1
5
Hg^{++}
CH$_3$HgX
7
7
4
Hg^{++}
Sediment
CH$_3$HgX
2
1
5
6
6
Hg^0
1 - Oxidation
2 - Reduction
3 - Volatilization
4 - Methylation
5 - Demethylation
6 - Sediment-Water Exchange
7 - Flow

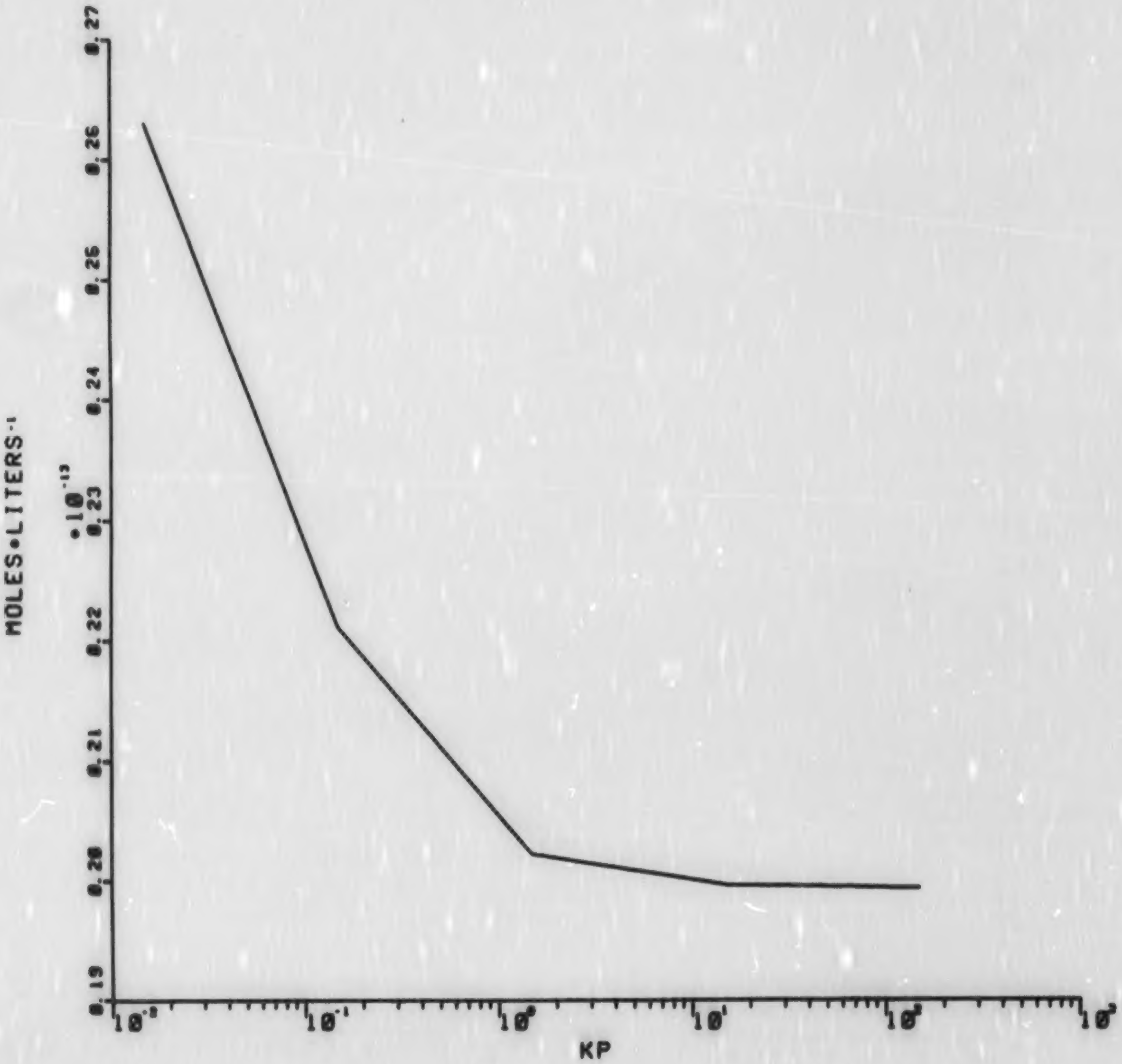
SCHEMATIC REPRESENTATION OF THE COMPONENTS, TRANSFORMATIONS, EXCHANGES AND TRANSPORT PATHWAYS REPRESENTED IN THE MODEL.

FIGURE 2



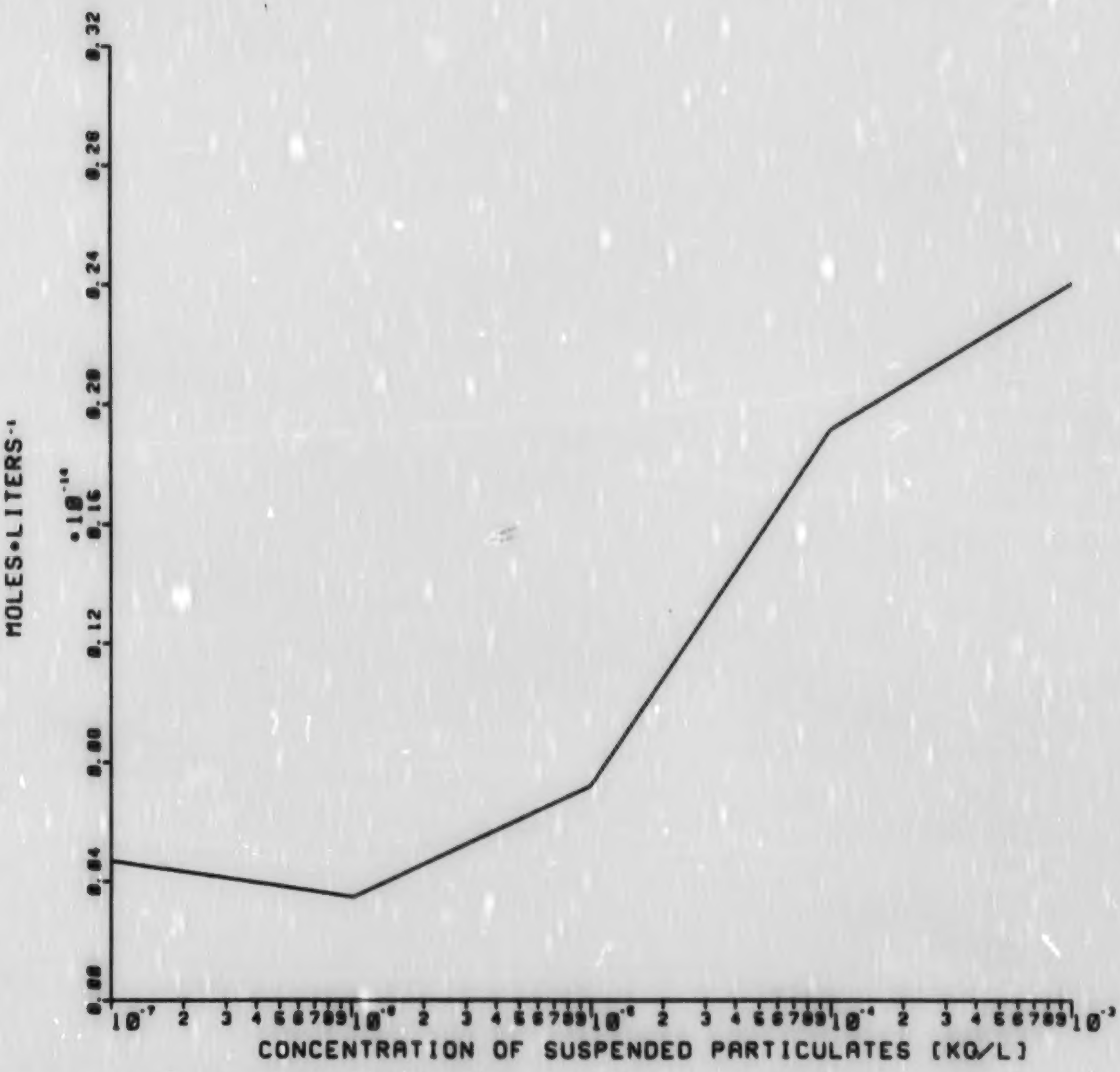
CH3HOX IN WATER AS A FUNCTION OF KP

Figure 3



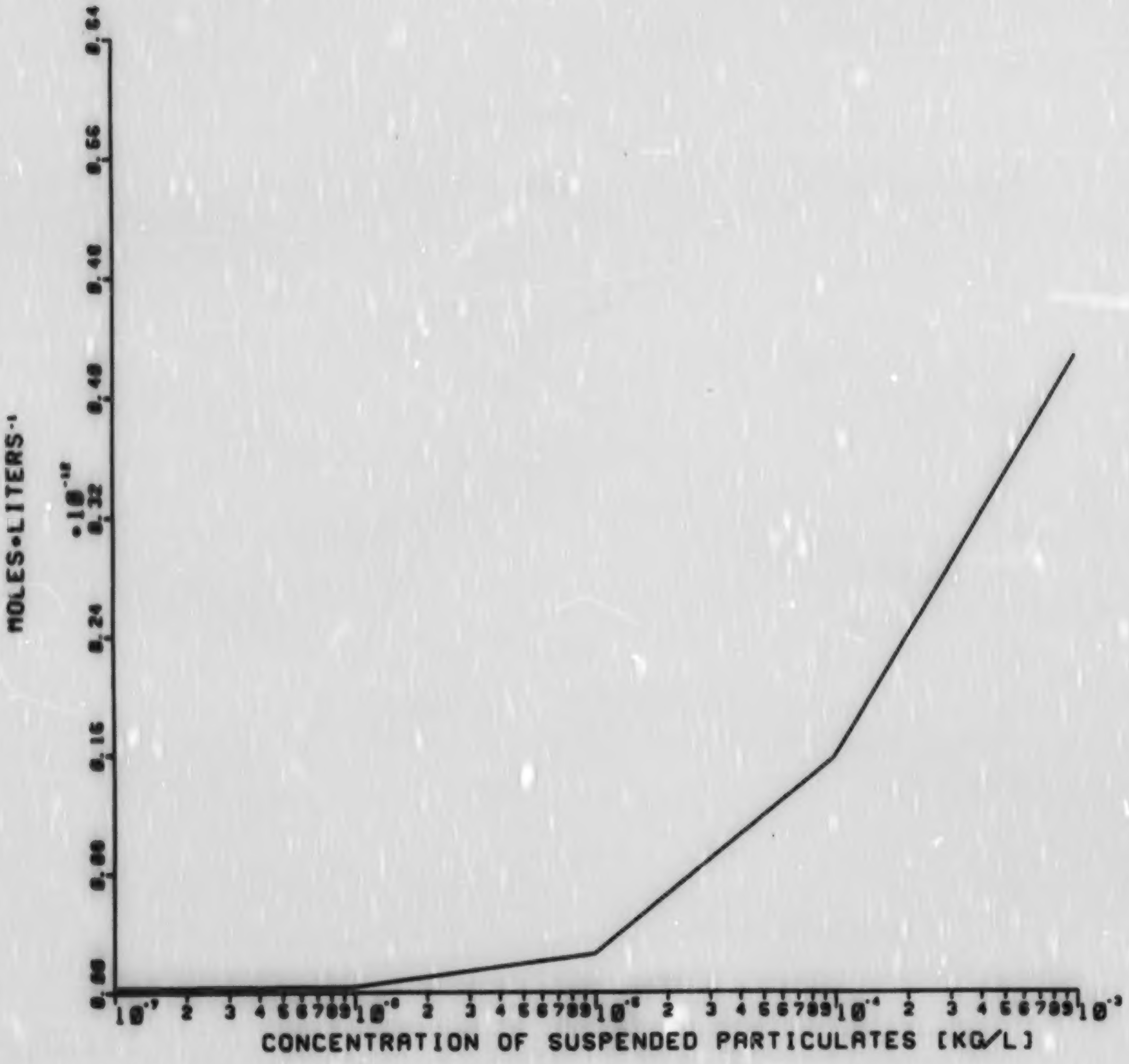
CH3HOX IN SEDIMENT AS A FUNCTION OF KP

FIGURE 4



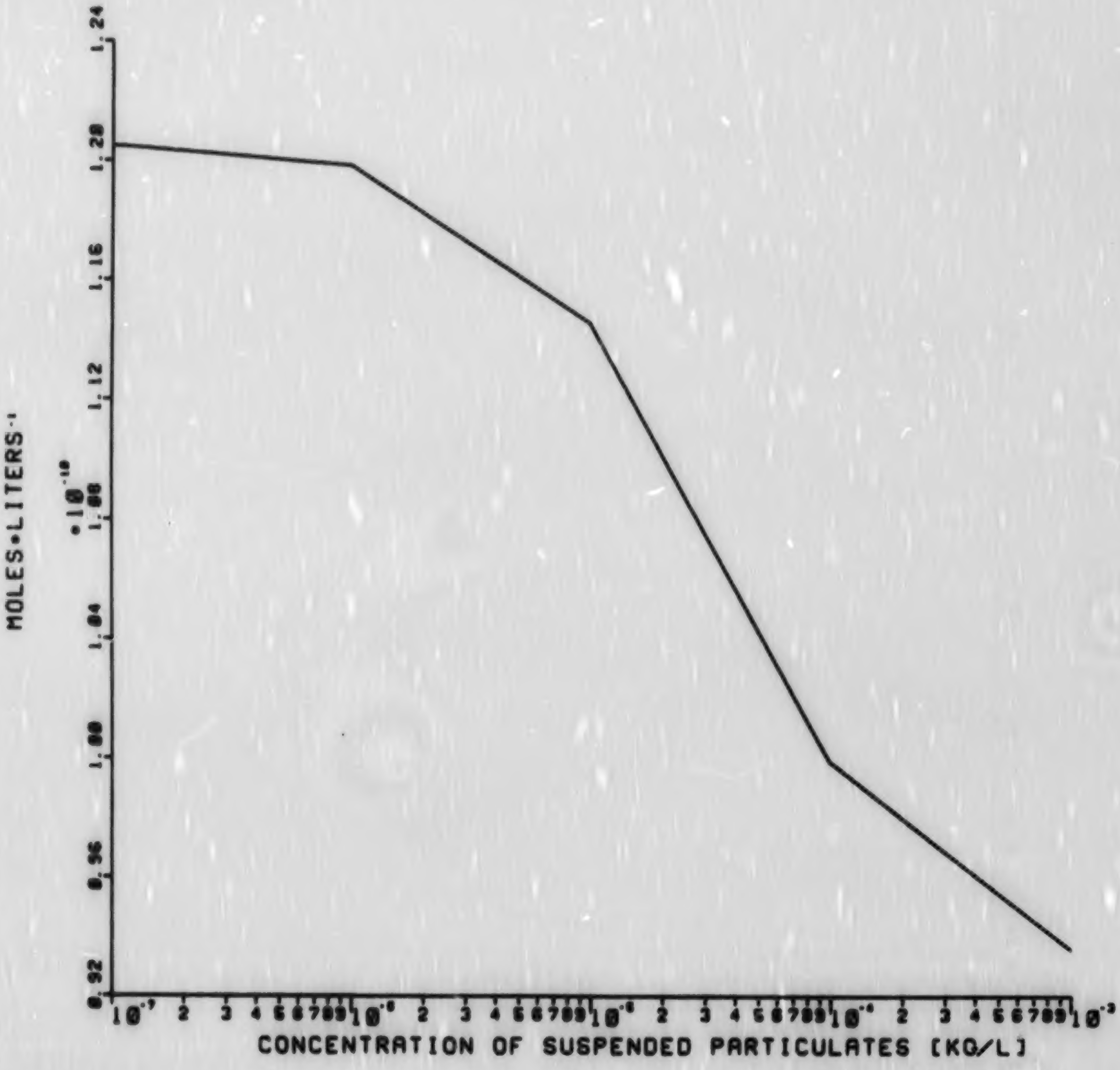
CH3HGX IN WATER AS A FUNCTION OF SUSPENDED PARTICULATES

FIGURE 5



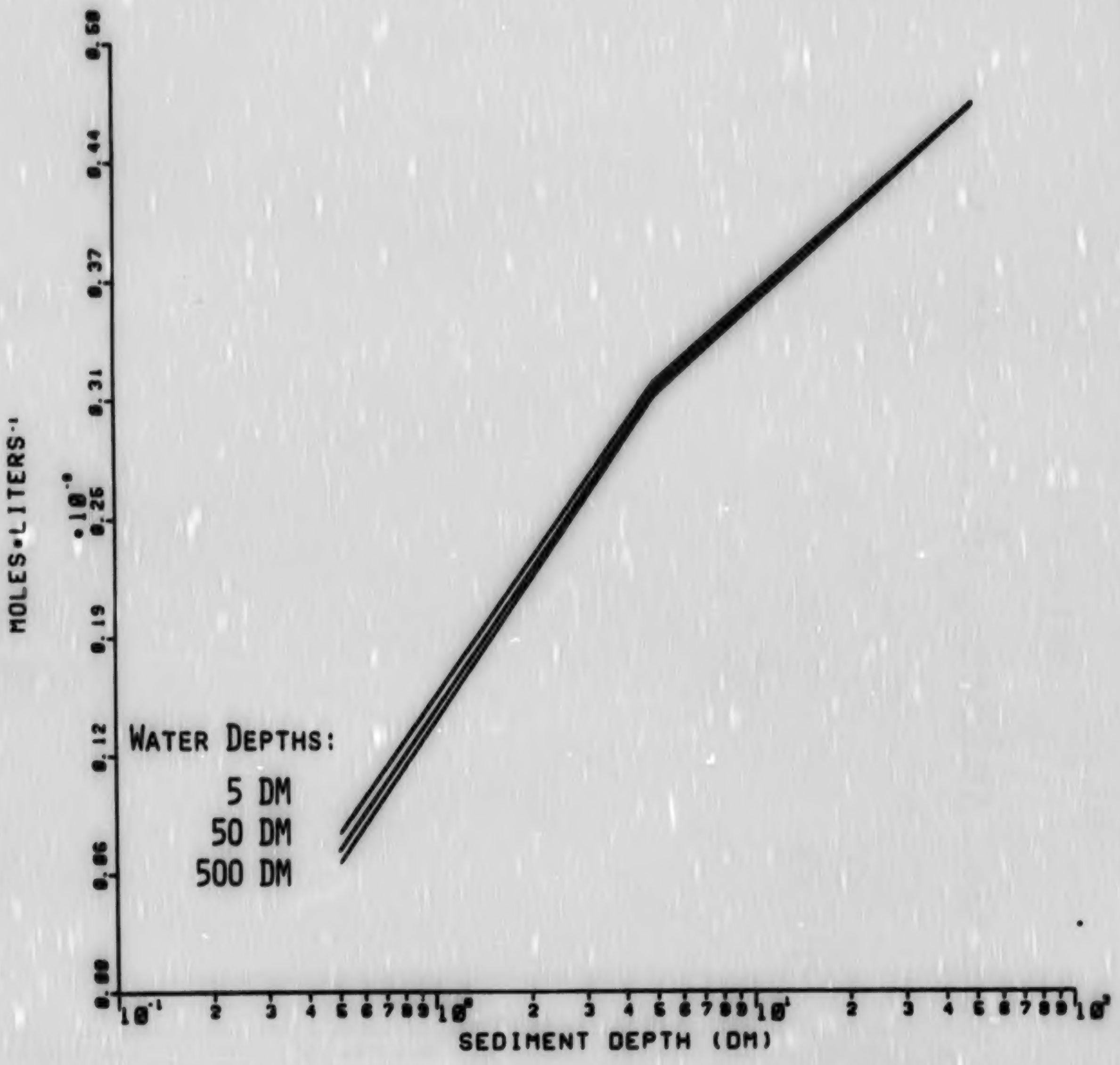
CH3HGX IN SEDIMENT AS A FUNCTION OF SUSPENDED PARTICULATES

FIGURE 6



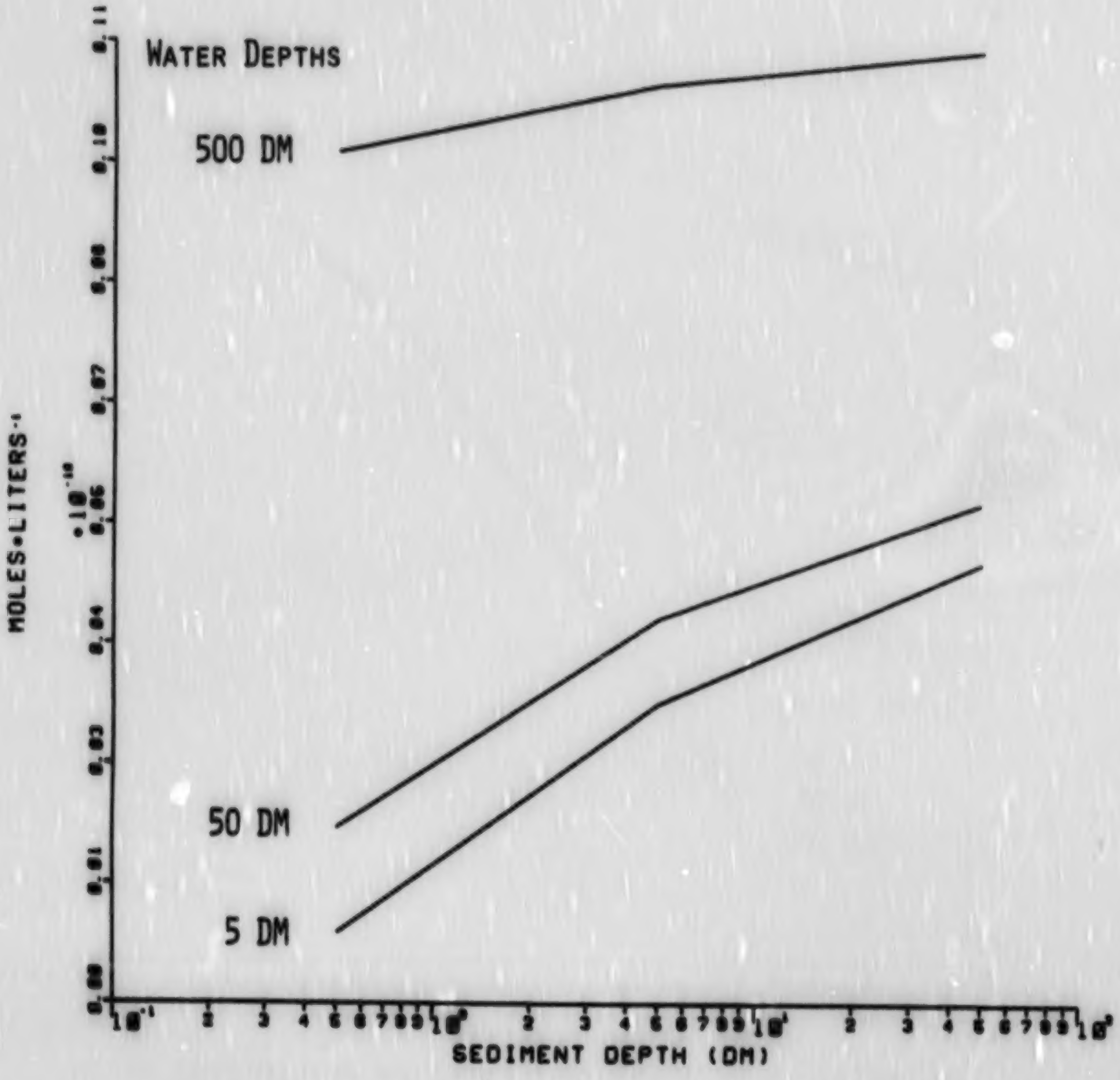
HG[0] IN SEDIMENT AS A FUNCTION OF SUSPENDED PARTICULATES

FIGURE 7



HG[0] IN SEDIMENT AS A FUNCTION OF SEDIMENT DEPTH
FOR VARYING DEPTHS OF WATER

FIGURE 8



HO[0] IN WATER AS A FUNCTION OF DEPTH OF SEDIMENT
FOR VARYING DEPTHS OF WATER

PREDICTION OF SOLUBILIZATION OF HYDROPHOBIC ORGANIC COMPOUNDS IN WATER

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I. INTRODUCTION

The role played by the partition coefficient (model system, octanol/water) in bioaccumulation and, therefore, in biological transport, is fairly well established.[1] In fact, it would appear to be the dominant variable. In *non*-biological transport (NBT) many more factors must be considered, as is evident from the topics of this symposium. But again, partitioning between phases or the closely allied phenomenon of adsorption to a hydrophobic surface[2,3] is assuredly going to play an important role.

A. Solubility

1. Of Solids: Studying the solubility of solid, hydrophobic organic chemicals, even in simplified model environments, is likely to prove more difficult than it is rewarding for the demands imposed by either the kinetic or the equilibrium approach in most cases make even a gross approximation difficult. There are some exceptions; a sizable quantity of insecticide and fungicide, for example, is currently being applied in the form of a wettable powder. In all probability, some of it may begin its dispersion into the environment without ever passing into solute form. Rates of solution and ultimate solubility of the crystalline form of the active material would be of far less value than the same parameters measured on the highly dispersed solid phase. Even in this example, however, it is probable that a "random walk" *partitioning* process - solution in water/adsorption on hydrophobic surface/solution in water/solution in lipid phase/etc. - will ultimately be responsible for any sizable movement of the pollutant away from its source.

2. Of Liquids: The process of dissolving an organic liquid in water is closely analogous to its partitioning between a lipid phase and water. In fact, when the organic liquid is not miscible with water, it can be considered a process of self-partitioning. Hansch *et al.*[4] have shown that the solubility of a wide variety of nonpolar and partially polar organic liquids is related to their log $P_{(oct)}$ values by this relationship:

$$\log 1/S = a \log P + b \quad (1)$$

	Slope a	Intercept b	n	r	s
All Solute Types	1.339	-0.978	156	0.935	0.472
All Except Alkanes	1.214	-0.850	140	0.955	0.344
Alkanes	1.142	-0.644	16	0.953	0.198

where n = number of data points, r = coefficient of correlation, and s = standard deviation.

There is one very important difference between solubility and partitioning measurements, especially as they apply to certain of the very hydrophobic compounds. Since the chlorinated hydrocarbon insecticides (including DDT) and also the polychlorinated biphenyls (PCBs) are involved, this difference may indeed be critical.

Solubility measurements are made in pure water and, even at saturation, the effects of one solute molecule on another are almost nil. However, when a solute such as pentachlorophenol is distributed between mutually saturated water and octanol phases, the 10^{-3} M octanol in the polar phase is considerably above the concentration of the phenol which can be expected to dissolve in pure water. Although small, this amount of octanol can help solubilize certain types of structures giving them a lower apparent hydrophobic character than would be predicted.

What is remarkable, however, is that *transport* phenomena in many biological systems and measurements of *bioaccumulation* in trout[1] are predicted much better by using log $P_{(oct)}$ than by using a solubility parameter. This will be covered in greater detail later.

B. Altered Solubility

Of course many pollutants are not accidental contaminants but, like insecticides and herbicides, are purposely used and applied. They are considered pollutants as soon as they "escape" from their intended target area. A rather frightening observation is that frequently, in aerial application, less than half the material applied actually strikes the target area! Be that as it may, the solubility and initial partition behavior of many of these are markedly altered to increase functionality. For instance, most lipophilic insecticides and herbicides are applied as emulsions which are much more rapidly dispersed into the aqueous phase of the environment. The chlorinated hydrocarbons used in machine cutting oils are another example of a potential pollutant whose properties are significantly altered through emulsification.

Yapel has measured the log $P_{(oct)}$ for 15 trifluoromethane sulfonanilide preemergence herbicides in the presence and absence of 0.1% Tween-80 (polyoxyethylene-20-sorbitan-monooleate). This work showed that T-80 did cause a lowering of observed lipophilicity of each member of the series but it was not evident how to relate the amount of lowering to the structural features of the herbicide-surfactant combination. Nor was there any attempt to determine how long this effect could be expected to persist in actual environmental conditions. There is a clear and obvious need for further carefully planned research in this area.

II. STRUCTURAL BASIS FOR SOLUBILITY AND PARTITIONING OF ORGANIC LIQUIDS

Reference to the close relationship between solubility and partitioning of organic liquids was made earlier. Recent attempts[6-9] to put one or both on a sound structural basis appear to be making progress.

Briefly stated, both solution and partitioning are equilibrium processes which depend very largely, in the case of apolar solutes, on the *size* of the cavity needed to accommodate the molecule and upon the *amount* of solvent structure (clustering) it induces in the surrounding water molecules (Figure 1a,b). If the solute contains a permanent localized dipole or formal charge, solvent clustering around that part of the cavity will be reduced and the reduced entropy decreases hydrophobicity. Hydrogen bonding groups in the solute likewise reduce this entropy effect and also reduce the net energy needed for cavity formation. Each of these effects will be elaborated on and their relationship to the rules governing the calculation of log P values pointed out.

A. Charge Separation Effects and Hydrogen Bonding

The addition of a "polar" or "hydrophilic" group to an otherwise apolar solute increases its water solubility and decreases its partition coefficient (oil/water by common usage). There appear to be two separate mechanisms - one depending upon a dipole and the other on hydrogen bonding - for the decrease in partition coefficient when a -Cl or an -OH is added to an alkane; but both must operate to some extent through their cluster breaking properties.

In Figure 1c, the water molecules in the section of the cavity wall near the -Cl orient themselves according to the *localized* charge separation present in the C-Cl bond. This solvent orientation is *structure-breaking* as far as water clustering is concerned. Of course, the dipole-dipole bond adds more stability than just London forces operating between water and hydrocarbon.

Much the same argument holds in Figure 1d where the polar group is -OH. Even though water clustering is dependent upon hydrogen bonds, the hydrogen bonds between solvent and solute (HB_{U-W}) must be considered as *structure-breaking* rather than structure-reinforcing as will be seen later.

B. Proximity Effects

1. Dipole Screening: A chlorine atom is larger than a hydrogen so, as expected, CCl_4 has a higher log *P* than does CH_4. Log $P_{(CCl_4)} = 2.83$ and log $P_{(CH_4)} = 1.09$; $\pi_{(Cl)} = 1.74/4 = +0.44$. As is seen in Figure 2a and 2b, both CCl_4 and CH_4 appear to expose an uninterpreted hydrophobic surface to the aqueous phase. However, in the case of methyl chloride (Figure 2c, log $P = 0.91$), the charge separation in the C-Cl bond is exposed and the combination of a smaller structured water "sweater" and the solute-solvent dipole-dipole attraction reduces $\pi_{(Cl)}$ from +0.44 to -0.18. This effect will be taken into account in the calculation procedures which follow as a multiple-halogenation correction.

The *difuse* dipole in *aromatic* halides apparently cannot act in the structure-breaking (hydrophilic) manner because $\pi\text{-Cl}/C_6H_5 = +0.71$ (*vs* +0.44 for alkane). It should be noted that, because it does not measure *localised* charge separation, dipole moment is *NOT* an indicator of the hydrophilicity imparted by cluster breaking. For example, in the di-chlorobenzene isomers, the ortho and para forms are essentially equally hydrophobic: log *P*-ortho = 3.38, $\mu = 1.58D$; log *P*-para = 3.39, $\mu = 0.0D$.

2. Cluster-Breaking Overlap: If two cluster-breaking (hydrophilic) groups are placed in close proximity (separated by no more than two carbon atoms), their effects overlap and thus are not additive; see Figure 3. This was first incorporated into a calculation scheme by Nys and Rekker.[10] At present, it seems adequately accounted for by assigning one of two correction values, depending on whether one or two methylene groups separate a wide variety of hydrogen bonding groups.

III. CALCULATION PROCEDURE

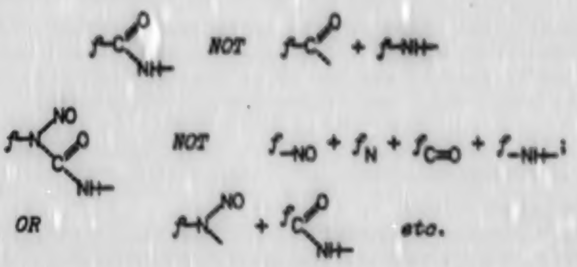
Partition coefficients can best be calculated in the form of their logarithms. All of the following are based on the octanol/water system but conversion to other solvent systems is possible by means of suitable regression equations.[11] [12] The original system of log *P* calculation,[13] based on the addition of a π constant to the known log *P* of a parent compound, is the simplest and most dependable to use when the data are available. However, even when using the largest list of log *P* values available at the present time - over 10,000 structure-sorted values[14] - one soon learns that a large number of environmentally interesting molecules are absent and not even any close analogs have their log *P*s reported. Therefore, the calculation method presented here will be based on the summation of hydrophobic "fragment constants" and certain other "factors" arising out of the constitutive nature of this parameter.

In a manner similar to Nys and Rekker's original proposal,[10] log *P* is calculated as:

$$\log P = \sum_{1}^{n} a_n f_n + bPe_1 + cPe_2 \tag{2}$$

where *f* is either a fragment or a factor and there are *a* number of each of *n* types of them; *b* is the number of hydrogen-bonding groups separated by only one methylene group and *c* is the number separated by two. It will be noted in Table I that $Pe_1 = +0.80$ and $Pe_2 = +0.40$.

Hydrophilic fragments cannot join one another; *i.e.*, the entire sequence of atoms must be considered as a single fragment. For example, it is:



The various polar fragments can be expected to interact in a different way with an aromatic fragment than with an aliphatic one. In every case, the aliphatic attachment is considered the "ground" state value and it is enhanced if the joined fragment is aromatic instead - doubly enhanced if two aromatic fragments join it. The enhancement is not uniform, however, and it is necessary to give separate listings for each type as will be noted in Table I as f, f^{ϕ}, and $f^{\phi\phi}$, respectively.

The need for constitutive factors in such calculations has been established previously.[15] These factors for chain and ring bonds, for chain and group branching, and for normal and conjugated multiple bonds are also given in Table I. The empirical formulae which allow for the extra hydrophobicity caused by multiple halogenation in aliphatic systems also appear.

Fujita[13] showed that the polar effect exerted by one aromatic substituent upon another often changes the hydrogen bonding of either group which in turn affects π or log P. For anilines and phenols this can be expressed in terms of Hammett's electronic parameter, σ:

	n	r	s	
$\Delta\Pi_{\text{X/aniline } vs \text{ benzene}} = 0.905\sigma_X + 0.16$	11	0.974	0.08	(3)
$\Delta\Pi_{\text{X/phenol } vs \text{ benzene}} = 0.823\sigma_X + 0.06$	24	0.954	0.10	(4)

This provides an equally good method for correcting aromatic *fragment* values for electronic interaction effects because it is evident that: $\Delta\Pi_X = \Delta f_X$. Even though it is a more precise correction, we presently need one which does *not* require knowledge of the various σ values. Thus we must compromise. In fact, we are experimenting with quite a number of compromises at the present time, several of which appear in Table I under the heading "Special Aromatic Fragment Types." The needs filled by these special values are:

(1) f^{1R} = fragment attached to α-carbon of aromatic ring side chain; this carbon has a slight aromatic character and therefore fragments attached to it have enhanced lipophilicity. It appears that this special type may be replaced by a constant correction of +0.13.

(2) f^{1X} = fragment attached either meta or para to $-NO_2$ group or in 3- or 4-position in pyridine. This may also apply when fragment in this relationship with any substituent having $\sigma_p \geq 0.5$.

(3) f^{2X} = fragment attached either ortho to $-NO_2$ or in 2-position of pyridine ring; can possibly be combined with f^{1X}.

In aliphatic systems, there can be a very large hydrophobic enhancement caused by halogenating the carbon atom adjacent to a hydrogen bonding group. The variation in group susceptibility to this polar effect is large (over 2.5 log units for the α-trifluoro- derivatives) and no predictive "rule" has been devised. The type of functional groups for which this effect has been studied appears in Figure 4. At present we have no alternative but to choose that hydrogen bonding substituent from these graphs which most closely resemble the one in question and then read off the $\Sigma\pi$ values for either mono-, di-, or tri-halogenation.

IV. CONCLUSIONS

Further research will likely bear out the early findings that hydrophobicity, as measured by log $P_{(oct)}$, is the most important parameter in bioaccumulation and biotransport; its role in non-biological transport may not be so dominant but should, none the less, be important. Some possibilities which may follow these findings are:

(1) The measurement of partition coefficients might be established as one requirement for registering a chemical (herbicide, insecticide, etc.).

(2) Projects could be encouraged or contracts proposed for partition coefficient measurement of basic classes of unregistered chemicals, taking care to avoid duplication of effort. As more measured values become available, the calculation procedures can be refined so that the number of structures for which neither measured nor calculated values are available will be rapidly reduced.

(3) The basic knowledge of the partitioning process can be applied to the design of chemical structures, or at least can direct a choice among various alternatives to one which should minimise any pollution problem.

To summarise: Partitioning is recognized as a vital physical process in the elaboration of transport phenomena of drugs and xenobiotics in living organisms and it seems safe to assume it will have no less important a role in that delicate "super-organism", the earth's total biosphere. Perhaps someday a partition coefficient will be measured and reported for every new compound as routinely as a boiling point or index of refraction. It may have greater ultimate significance.

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TABLE I. FRAGMENT CONSTANTS

		f	f^{ϕ}	$f^{\phi\phi}$	S.F.T.[1]
No Carbon					
No H	-Br	0.20	1.09		$f^{1R} = 0.48$
	-Cl	0.06	0.94		
	-F	-0.38	0.37		
	$-SO_2F$		0.30		
	-I	0.59	1.35		
	-N<	-2.18	-0.93	-1.13	$f^{1R} = -1.76$
	$-\overset{\vert}{\underset{\vert}{N}}\oplus-$	-7.37	-6.71		
	-NO		0.11		
	$-NO_2$	-1.16	-0.03		$f^{X2} = +0.09$
	$-SO_2N<$		-2.09		
	-O-	-1.82	-0.61	0.53	$f^{X1} = -0.22$ $f^{X2} = +0.17$
	-SO-	-3.01	-2.12	-1.62	
	$-SO_2-$	-2.40	-2.17	-1.28	
	$-OPO_3<$		-2.22		
	-S-	-0.79	0.03	0.77	
With H	-NH-	-2.15	-1.03	-0.09	$f^{X1} = -0.37$
	$-SO_2NH-$			-1.10	$f^{1/\phi} = -1.72$
	=NNH-	-3.06	-0.62		
	-OH	-1.64	-0.44		$f^{X1} = +0.32$ $f^{1R} = -1.34$
	-SH	-0.23	0.62		
	$-NH_2$	-1.54	-1.00		$f^{1R} = -1.35$ $f^{X1} = -0.23$
	$-SO_2NH_2$		-1.59		$f^{X1} = -1.04$
With Carbon					
No H	-CN	-1.27	-0.34		$f^{1R} = -0.88$
	-CON<	-3.04	-2.80	-1.93	$f^{1/\phi} = -2.20$
	-SCN	-0.48	0.64		$f^{1R} = -0.45$
	-CO-	-1.90	-1.09	-0.50	$f^{1R} = -1.77$ $f^{X1} = -0.83$
	$-CO_2-$	-1.49	-0.56	-0.09	$f^{1R} = -1.38$ $f^{X1} = -0.36$
	$-\bar{C}O_2-$	-5.19	-4.13		
With H	-CONH-	-2.71	-1.81	-1.06	$f^{1/\phi} = -1.51$
	>C=NOH	-1.25	-0.38		
	-OCONH-		-1.51		$f^{1/\phi} = -0.91$
	-C=O(H)		-0.42		
	$-CO_2H$	-1.11	-0.03		$f^{1R} = -1.03$

In Aromatic Ring

-N=	-1.08
-N-	-0.52
-N+=	-6.59
-NH-	-0.67
-O-	-0.08
$-N\overset{O}{\diagup}-$	-3.46
-S-	0.38
$-S\overset{O}{\diagup}-$	-2.08
-Se-	0.45
$\underline{C}$	0.13
$\underline{\hat{C}}$	0.225
$\underline{\overset{*}{C}}$	0.44
$\underline{CH}$	0.355
$-\underline{C}O_2-$	-1.40
$-C\overset{O}{\diagup\!\!\diagup}-$	-1.10
$-C\overset{O}{\diagup\!\!\diagup}NH-$	-2.00

Double Bonds

Normal	-0.55
Conjugated to ϕ	-0.40
Conjugated to -C=O	-0.08
Conjugated to -O-	+0.15

Triple Bonds

Normal	-1.42

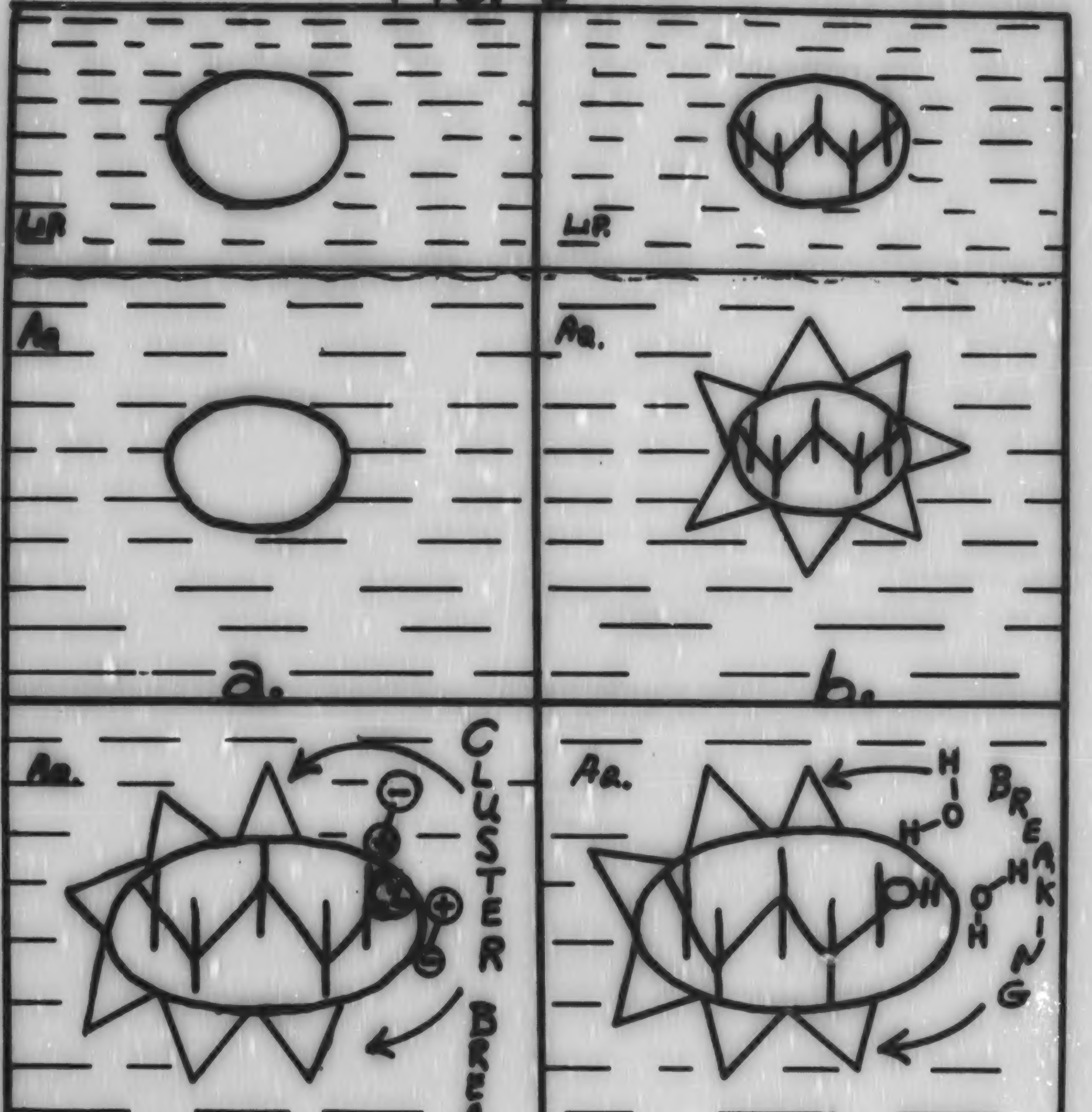
Factors

Chain Bonds = -0.12 (n-1)
Ring Bonds = -0.09 (n-1)
Ring Cluster = -0.45
Chain Branch = -0.13
Group Branch = -0.22

Halogenation[2]

Multiple:
gem- 2 = 0.30; 3 = 0.53; 4 = 0.70
vic- 2(n-1) × 0.14

Fig. 1



L.P.
L.P.
Aq.
Aq.
a.
b.
Aq.
Aq.
CLUSTER BREAK.
H O H
H O H
BREAKING
OH
c.
d.

SOLVATION ENERGY AS AFFECTED BY SOLUTE VOLUME AND WATER STRUCTURE

a. Cavity in partitioning solvents
b. Cavity with solute present
c. Solute with polar group
d. Solute with hydrogen bonding group

-CONH$_2$	-2.18	-1.26		{f^{1R} = -1.99 f^{X1} = -0.84
-NHCONH-		-1.57	-0.82	

---

[1] See text for definition of f^{1R}, f^{X1}, f^{X2}; Special Fragment Types: for unsymmetrical bi-functional groups, the primary attachment considered that of later WLN symbol; *i.e.*, the *left*-hand bond in structures as shown; the reverse given by 1/ϕ. [2] *Not* affecting H-bonding group.

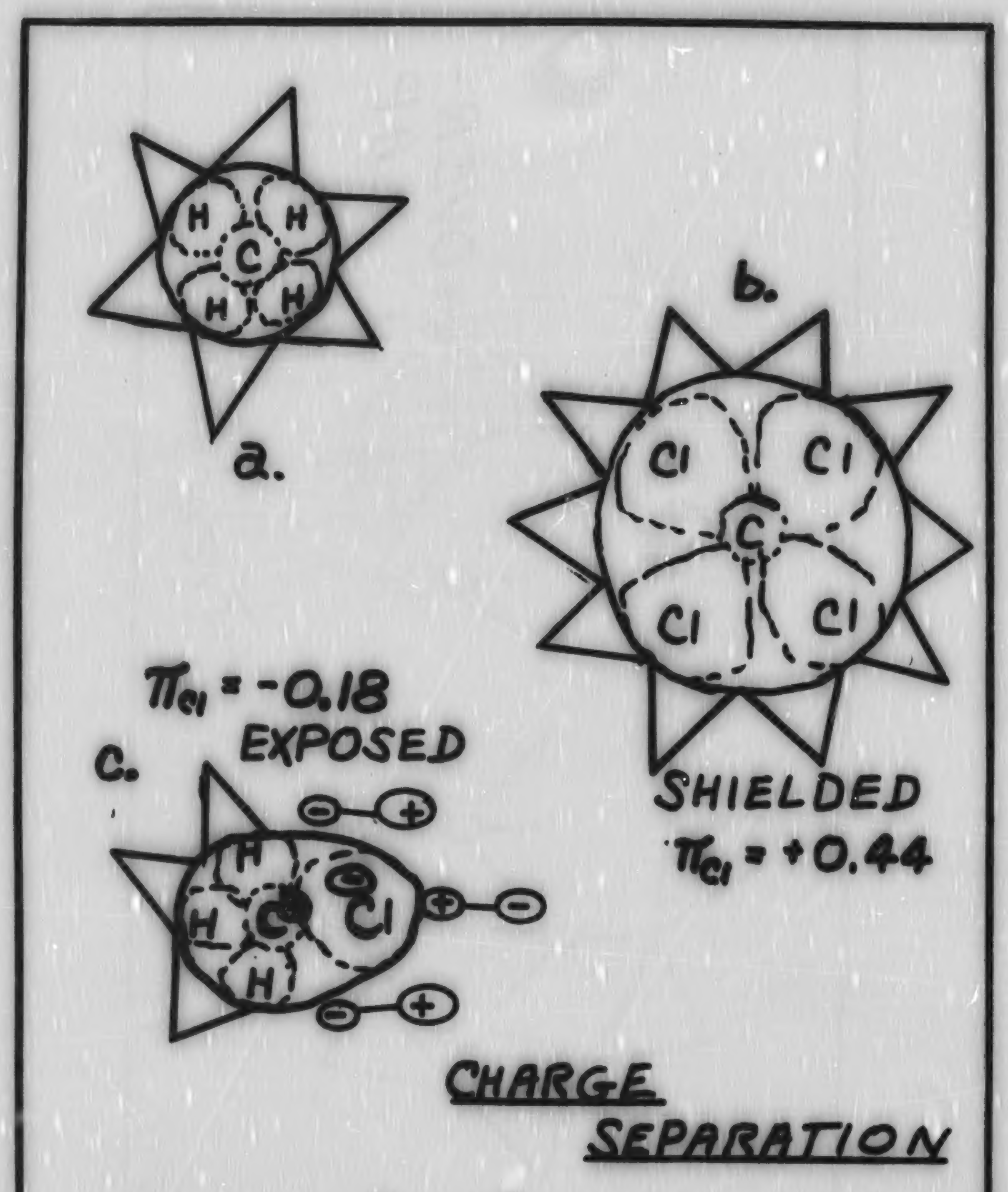

H
H
C
H
H
a.
b.
Cl
Cl
C
Cl
Cl
$\pi_{Cl} = -0.18$
EXPOSED
c.
H
H
C
Cl
H
SHIELDED
$\pi_{Cl} = +0.44$
CHARGE SEPARATION

FIG. 2.

CHARGE SEPARATION IN ALKYL SOLUTES
a. No charge
b. Charge, shielded
c. Charge, exposed

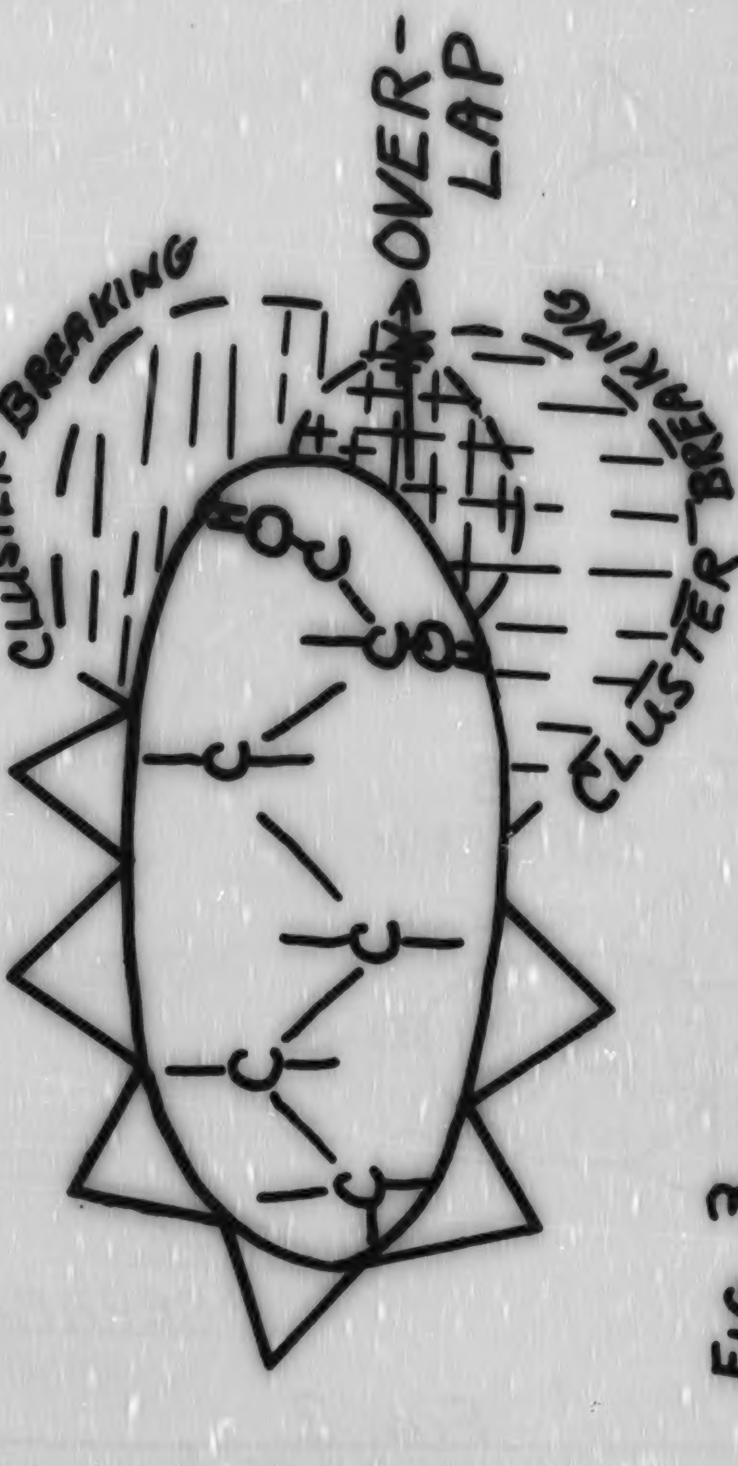
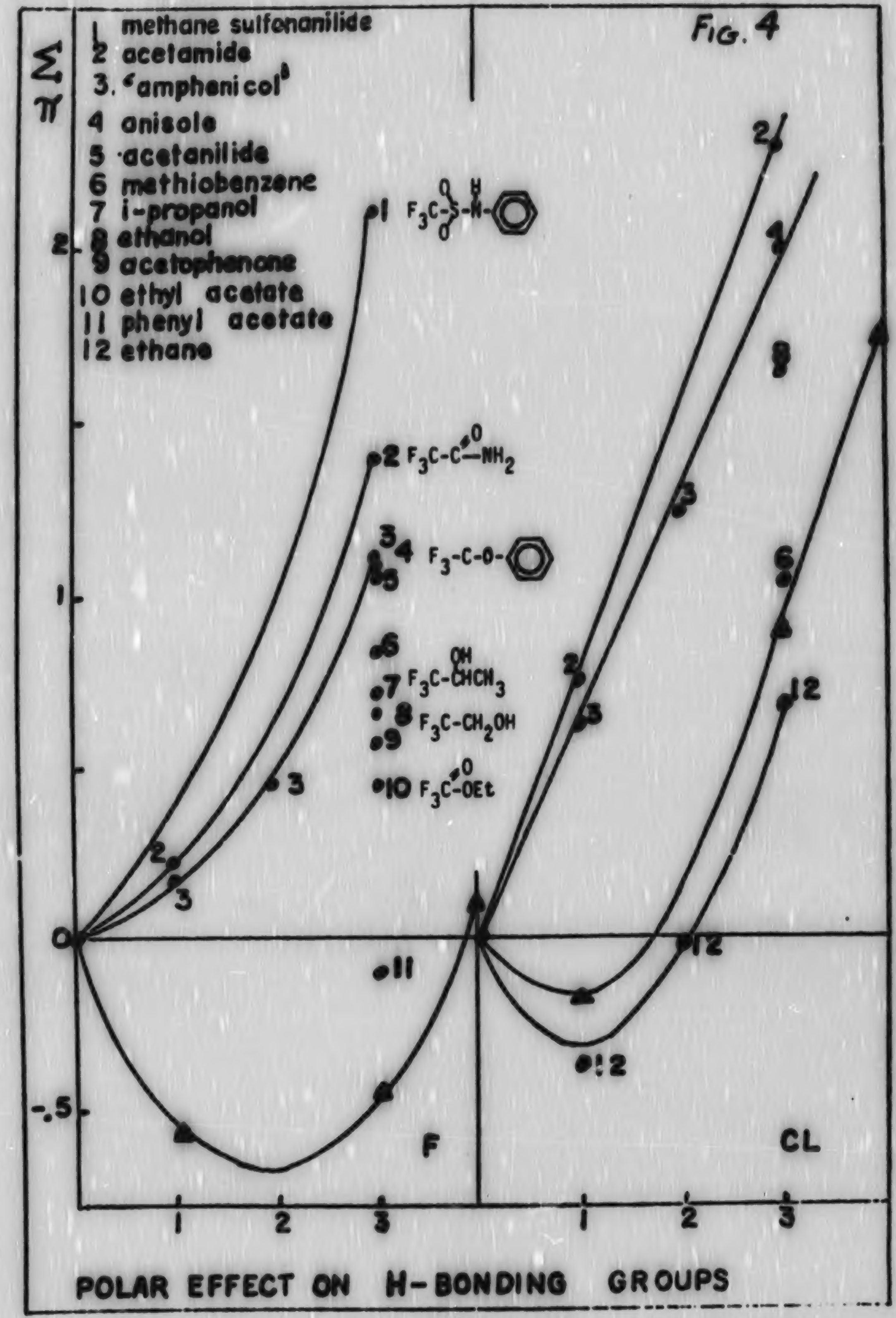

CLUSTER BREAKING
OVER-
LAP
CLUSTER BREAKING

FIG. 3

PROXIMITY EFFECT RESULTING FROM CLUSTER BREAKING OVERLAP

FIG. 4



POLAR EFFECT ON HYDROGEN BONDING EFFECT IN ALKYL STRUCTURES

THE ENVIRONMENTAL PHOTODEGRADATION OF SELECTED ORGANOMETALLIC COMPLEXES

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Kodak Park
Rochester, N.Y. 14650

Introduction

Synthetic chelating agents are being used in agriculture, food and drug processing, photography, and textile and paper manufacturing. The combined United States production of one such chelating agent, the polyamine polycarboxylic acid EDTA, was 64 million pounds in 1972 (1). Any study of the fate of EDTA and similar chelating agents in the environment must be, in fact, a study of the various chelates formed between the common metal ions and the chelating agents. This is a direct result of the concentration of common metal ions in natural waters (2) and the magnitude of the corresponding chelate formation constants (3).

Interaction with sunlight, i.e. photodegradation, may act to remove these chelates from the environment. Previous studies on the photodegradation of Fe(III)-EDTA, one of the most thermodynamically stable EDTA chelates, have identified carbon dioxide (from the carboxyl carbon) formaldehyde (from the acetate carbon), and Fe(II) as products in a 1:1:2 ratio (4,5). Studies on the photodegradation of ferric NTA, an aminopolycarboxylic acid - metal chelate, by Trott *et al.* (6) have identified these same photodegradation products along with iminodiacetic acid (IMDA).

In our studies, we have investigated the rates of photodegradation of buffered aqueous solutions of X(N)-carboxyl-^{14}C-labeled EDTA in the presence of oxygen and simulated sunlight. Also, the identification of additional ferric EDTA photodegradation products N-carboxymethyl-N,N'-ethylenediglycine [ED3A], N,N'-ethylenediglycine [EDDA-N,N'], N-carboxymethyl-N-aminoethyleneglycine [EDDA-N,N], IMDA, N-aminoethylene [EDMA], and glycine is reported; the structure of these materials is given in Figure 1. These degradation products have been quantified and their generation studied kinetically from pH 4 to pH 8, the pH range of natural waters (6).

Materials and Methods

Static photolysis of X(N)-1-^{14}C-EDTA chelates was performed in a modified 50 ml PYREX Erlenmeyer flask. This flask was fitted with a downward curving 3/4" diameter side arm threaded to receive a scintillation vial containing a CO_2 absorber of 1.0 ml of diethanolamine and 0.2 ml of water attached by a threaded TEFLON brand of polytetrafluoroethylene sleeve. The chelate was formed *in situ* at 0 time by adding stoichiometric amounts of the cation chloride and a solution of 1-^{14}C-EDTA to 50 mM sodium acetate buffer at pH 4.5. All solutions were prepared in sterile water. The final chelate concentration was 1.67 mM. Flasks were sealed with serum stoppers and irradiated at 4000 foot-candles for 100 hours by a 5500 watt xenon arc lamp with a UV transmissive filter. Fresh scintillation vials were attached at appropriate intervals, and 5 ml of 6 *N* HCl was injected through the stopper at the end of the experiment to release any dissolved carbon dioxide. A scintillation cocktail consisting of toluene and methoxyethanol was added to the vials and the amount of radioactivity volatilized from the flasks was assayed. Triplicate determinations were done in all cases. The EDTA chelates studied in this manner were Na(I), Mg(II), Ca(II), Mn(II), Fe(III), Co(II), Cu(II), Zn(II), Cd(II), Ni(II) and Hg(II). Formaldehyde in flask contents after photodegradation was assayed spectrophotometrically using the chromotropic acid method (7). The photodegradation study of Fe(III)-1-^{14}C-EDTA was repeated at pH 4.5, pH 6.9 (50 mM sodium acetate buffer), and pH 8.5 (50 mM ammonium chloride buffer), with eight replicate flasks used for each pH value. Flasks were successively removed over a 96-hour period for analysis of the flask contents for bacteria and the products of photodegradation.

Volatile N-trifluoacetyl—n-butyl esters of EDTA and its photodegradation products were prepared by the method of Zumwalt *et al.* (8). Standard curves were prepared by gas chromatography for EDTA, ED3A, EDDA-N,N', EDDA-N,N, IMDA, NTA, EDMA, and glycine using 4-aminobutyric acid as an internal standard. Gas chromatographic analysis of these volatile esters was performed on 3% QF-1 on Gas-Chrom Q, programming from 110-260°C at 10°/min.

The N-trifluoroacetyl—n-butyl esters of EDMA and EDDA-N,N as photodegradation products of Fe(III)-EDTA, were identified by fragmentation pattern analysis on GC-MS. The identities of other photodegradation products were determined by comparison to reference materials whose mass spectrometric properties had been established by Belly *et al.* (9).

Results

Of the EDTA chelates surveyed, only those of manganese, iron and cobalt photodegraded at pH 4.5 to produce $^{14}CO_2$ and formaldehyde. The $^{14}CO_2$ evolution versus time curve for these three cations is shown in Figure 2.

Some of the results of the in-depth studies on Fe(III)-1-^{14}C-EDTA are given in Figure 3. Photodecarboxylation was pH dependent, with the greatest amount of $^{14}CO_2$ evolution occurring at pH 4.5. Similarly, the rate of Fe(III)-EDTA disappearance as determined by gas chromatography was most rapid at pH 4.5, as shown in Figure 3; no Fe(III)-EDTA was detectable after 24 hr of irradiation at pH 4.5 or pH 6.9, and none was detectable after 32 hr of photolysis at pH 8.5. Figure 3 also shows that significant photodecarboxylation was evident even after Fe(III)-EDTA was no longer detectable at all the pH values tested.

ED3A, EDDA-N,N', EDDA-N,N, EDMA, IMDA, and glycine were identified as photodegradation products by GC-MS or by comparison with known materials. Formaldehyde was identified as a photodegradation product at all pH levels studied but was not quantitated since the amounts of formaldehyde in the CO_2 absorbers could not be measured. No NTA was detected during the course of the experiment nor were any other unidentified peaks found on the gas chromatograms. Bacterial counts were insignificant.

After 96 hr of photolysis at pH 4.5 no ED3A, EDDA-N,N', or EDDA-N,N was detectable; EDMA and lesser amounts of IMDA and glycine were the only photodegradation products remaining. All photodegradation products remained after 96 hr of Fe(III)-EDTA photolysis at pH 6.9; at this pH, IMDA and EDMA were found at approximately the same concentrations at the end of the experiment. At pH 8.5, the photolysis of Fe(III)-EDTA gave rise to all the photodegradation products found at pH 4.5 and pH 6.9, but at a slower rate than at the lower pH values. Comparisons of the concentrations of EDDA-N,N' and EDDA-N,N vs. time at any pH value tested indicate that there was no preference for the generation of one of these two EDDA isomers over the other as a photolysis product of Fe(III)-EDTA. The material balance in terms of % nitrogen and % carbon atoms recovered indicates that all major photodegradation products have been identified during these experiments.

Discussion and Conclusions

These studies on the photodegradation of EDTA chelates in aqueous solution have given insight into the fate of EDTA when discharged to the environment. Our results, which indicated a photosensitivity of only the EDTA chelates of Mn(II), Fe(III) and Co(II) out of all of those tested, agree with the firdings of Natarajan and Endicott (4), who found the EDTA chelates Fe(III) and Co(II) were photosensitive and those of Cr(III), Ni(II) and Cu(II) were not. These results for Cu(II)-EDTA contrast with those reported for Cu(II)-NTA by Langford *et al.* (10) who reported a significant photodecomposition of this chelate. The production of ED3A, CH_2O and CO_2 from the photolysis of EDTA reported here along with the generation of CO_2, CH_2O and IMDA as products of Fe(III)-NTA photodegradation reported by Trott *et al.* (6) suggest a similar mechanism may be involved in the photodegradation of these Fe(III) chelates.

The results of Fe(III)-EDTA photodegradation suggest a possible scheme, presented in Figure 4. This is based on the time the various photodegradation products were first detected and on their relative concentrations. As mentioned above, IMDA has been shown to be a product of the photodegradation of Fe(III)-NTA. However, our results indicate that NTA is not a significant photodegradation product of Fe(III)-EDTA, so IMDA generation would appear to be a result of ED3A photolysis.

Although bacterial metabolism was excluded in these experiments, the biodegradation of IMDA, EDMA, EDDA-N,N', EDDA-N,N and ED3A have been recently observed (9). If we base conclusions on the results of these biodegradation studies, the products of the various photodegradation reactions of Fe(III)-EDTA would also be biologically degraded in a natural environment, thus decreasing the probability of photolysis product buildup in natural waters.

It is concluded that photodegradation may play a significant role in the removal of Fe(III)-aminopolycarboxylic chelates such as Fe(III)-EDTA and Fe(III)-NTA from natural waters.

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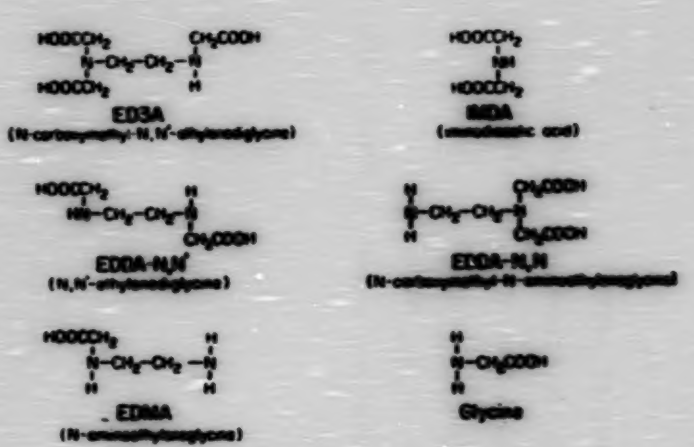
EDSA
(N-carboxymethyl-N,N'-ethylenediglycine)
IMDA
(iminodiacetic acid)
EDDA-N,N'
(N,N'-ethylenediglycine)
EDDA-N,N
(N-carboxymethyl-N-aminoethylglycine)
EDMA
(N-aminoethylglycine)
Glycine

Figure 1

Photodegradation of Products of Fe(III)-EDTA

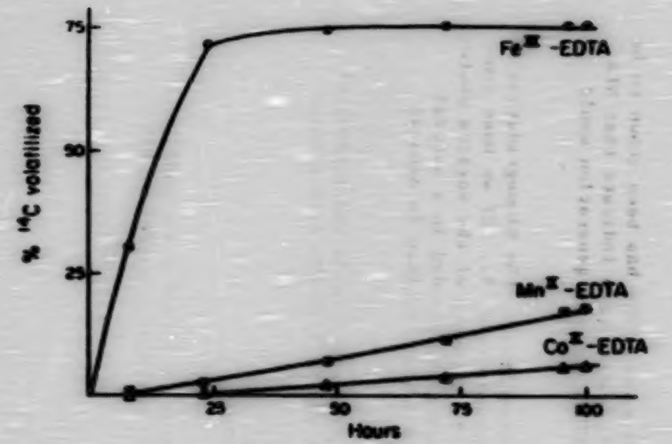

Figure 2

Scatic Photodegradation of Fe(III)-, Mn(II)-, and Co(II)-1-^{14}C-EDTA, pH 4.5, 4000 ft. candles

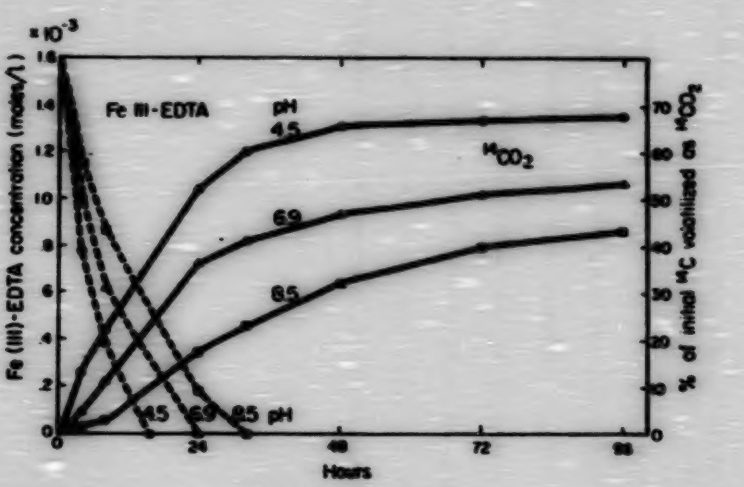

Figure 3

Concentration of Fe(III)-1-^{14}C-EDTA and Percent Initial ^{14}C Volatilized (4000 fc)

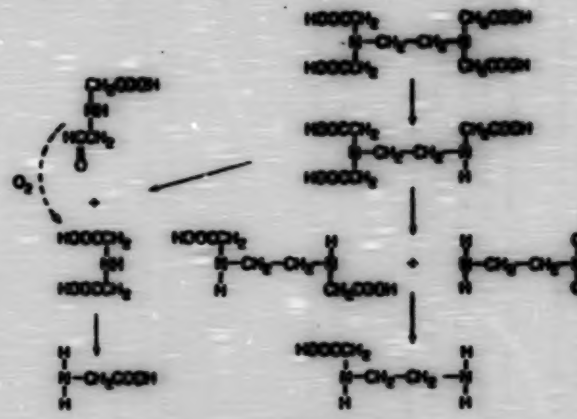

Figure 4

Proposed Photodegradation Scheme for Fe(III)-EDTA

KINETICS OF HYDROLYSIS AND OXIDATION OF ORGANIC POLLUTANTS IN THE AQUATIC ENVIRONMENT

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A wealth of information is available describing the detailed kinetics of hydrolysis, free radical and photochemical oxidation reactions under controlled and defined laboratory conditions. This knowledge can be used effectively to describe the hydrolytic degradation of organic pollutants in aquatic systems. Almost no detailed information is available, however, on the chemical oxidation reactions that occur in aquatic environments. This paper presents some general features of the kinetics of hydrolysis and free radical oxidations that are applicable toward understanding and evaluating the importance of these reactions in these environmental degradation processes.

Free Radical Oxidation

Oxidation of organic compounds in the environment almost never involves direct reaction of an organic molecule with oxygen; instead the oxidation requires the formation of intermediate radicals and/or excited species.

One of the most common and best understood oxidation processes involves peroxy and alkoxy radical chains (autoxidations) wherein three distinct types of radical processes are recognized: initiation, propagation, and termination. Most of the complications found in autoxidations are readily understood in terms of this chain process in which the two propagation reactions

$$RO_2\cdot + RH \xrightarrow{k_p} RO_2H + H\cdot \qquad (1)$$

$$RO\cdot + RH \xrightarrow{k_p'} ROH + R\cdot \qquad (2)$$

are mainly responsible for oxidation of the organic substrate. Reactions (1) and (2) are depicted here as H-atom transfer; they can also involve addition of radicals to double bonds such as in vinyl chloride or styrene.

The rate laws for these processes are

$$-\frac{dO_2}{dt} = R_{ox} = k_p[RH][RO_2\cdot] \text{ or } k_p' [RH][RO\cdot] \qquad (3)$$

and for $RO_2\cdot$ propagation

$$R_{ox} = \left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} k_p[RH] \qquad (4)$$

where R_i is the rate of radical formation and $2k_t$ is the rate constant for radical destruction.

In the environment, oxidation of a substrate (RH) would involve $RO_2\cdot$ or $RO\cdot$ radicals having many different kinds of structures, and the rate of oxidation (R_{ox}) is the sum of the individual rate expressions for oxidation by each kind of radical. If we make the simplifying assumption that all $RO_2\cdot$ or $RO\cdot$ radicals (primary, secondary, and tertiary) have about the same rate constant, k_p or k'_p (a reasonable assumption within a factor of ten), then we can use equation (5) to evaluate the lifetime of a compound in an oxidizing environment.

$$t_{\frac{1}{2}} = \ln 2/k_p[RO_n\cdot] \qquad (5)$$

$$n = 1 \text{ or } 2$$

We have estimated half-lives for a variety of organic compounds using a reasonable value for $[RO_2\cdot]$ of 10^{-8} M, and known values[1] of k_p for the reactive CH bonds at 30°. Table 1 summarizes these values.

Table 1

HALF-LIVES FOR REACTION OF $RO_2\cdot$ WITH C-H BONDS AT 30°C[a]

Compound	k_p 1/mol sec[b,c]	$t_{\frac{1}{2}}$, days
n-Alkanes (CH_2-)	0.00027	3×10^6
Branched alkanes (÷CH)	0.0048	1.7×10^5
Olefins (allylic-CH)	0.084	9.5×10^2
Benzyl (CH_2-)	0.10	8×10^3
Dienes (1,4-Allylic)	0.23	3.5×10^3
Alcohols (>CHOH)	0.009	8.9×10^4
Ethers (-O-CH_2-)	0.016	5×10^4
Aldehydes (-CHO)	3000[d]	6 hr

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[a] Calculated from equation (5) using $[RO_2] = 10^{-8}$ M.

[b] For reaction $\underline{t}\text{-BuO}_2\cdot + RH \rightarrow \underline{t}\text{-BuO}_2H + R\cdot$

[c] Reference 1.

[d] For reaction $RC(O)O_2\cdot + RCHO$.

The very long half-lives listed in Table 1 suggest that, for many organic compounds present in the environment, oxidation by $RO_2\cdot$ radicals will be unimportant unless $[RO_2\cdot]$ exceeds 10^{-4} M.

Reaction with Alkoxy Radicals

Although chain oxidation via $RO_2\cdot$ radicals is unimportant under environmental conditions, radical oxidation by $RO\cdot$ radicals is still possible because of their much higher reactivity; values for k'_p for the reaction

$$RO\cdot + RH \xrightarrow{k'_p} ROH + R\cdot$$

are in the range 10^3-10^5 liter/mol-sec.[1] Thus, half-lives for reaction of RO· with organic compounds can be quite short if a continuous source of RO· radicals is available. Table 2 lists estimated half-lives for different classes of organic compounds assuming $[RO\cdot] = 10^{-10}$ M.

Table 2

HALF-LIVES FOR REACTION OF RO· WITH ORGANIC C-H BONDS AT 40°C[a]

Compound	$k'_p \times 10^{-4}$ l/mol sec[b]	$t_{\frac{1}{2}}$, hours
Alkane ($-CH_2$)	3.6	52
Branched alkane (-CH)	13	14
Olefin (allylic-CH_2-)	24	7.2
Benzyl ($-CH_2-$)	11	14
Ethers ($-CH_2-$)	31	6.1
Ketone ($-CH_2-$)	0.6	320
Chlorocarbons-CHCl	0.5	380

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[a] Calculated from equation (5) using $[RO\cdot] = 10^{-10}$ M.

However, RO· and $RO_2\cdot$ chemistry generally are closely related. Under certain conditions RO· initiates the $RO_2\cdot$ chain sequence, and in other situations $RO_2\cdot$ can be converted to RO· by the reaction

$$2\,RO_2\cdot \longrightarrow 2\,RO\cdot + O_2 \qquad (6)$$

Although reaction (6) may not always be an important source of RO· radicals, some photochemical and metal-ion-catalyzed reactions could provide high concentrations of RO· radicals under environmental conditions. Photochemistry is frequently linked to environmental oxidation[2] and may be the most important general means by which reactive radical species like RO· are generated.

$$ROOH(ROOR) \longrightarrow RO\cdot + HO\cdot\ (2\,RO\cdot) \qquad (7)$$

$$>C{=}O \longrightarrow >\dot{C}{-}O\cdot \text{ (triplet)} \qquad (8)$$

Reaction (7) is simply homolysis of peroxides formed by radical or singlet oxygen reactions (see below). Although this process is not very efficient in the solar region where peroxides absorb weakly, it can contribute to the radical population. Reaction (8), which proceeds through an excited singlet, could be the most important environmental photooxidation reaction[*] because the triplet diradical has a reactivity similar to that of RO·.[3] Reaction with substrate can initiate the oxidation process, and the carbonyl is regenerated for further use by reaction with oxygen:

$$>\dot{C}-\dot{O} + RH \longrightarrow >\dot{C}-OH + R\cdot$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$>\dot{C}-OH + O_2 \longrightarrow >C{=}O + HO_2\cdot$$

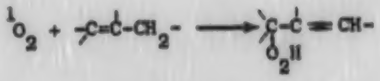
$$2HO_2\cdot \longrightarrow H_2O_2 + O_2$$

$$RO_2\cdot + HO_2\cdot \longrightarrow RO_2H + O_2$$

Peroxides may also be generated by formation of singlet oxygen ($^1O_2$),[4]

$$>\dot{C}-\dot{O} + {}^3O_2 \longrightarrow >C{=}O + {}^1O_2$$

and reaction of $^1O_2$ with olefins,[5]



$$^1O_2 + >C{=}\overset{|}{C}-CH_2- \longrightarrow >\underset{O_2H}{C}-\overset{|}{C}{=}CH-$$

Several transition metal ions, such as Fe and Cu, occur naturally in amounts sufficient to warrant consideration of their possible roles as catalysts for environmental autoxidation. Transition metal ions catalyse autoxidations and peroxide decompositions through the efficient cycle that forms RO· and RO_2[6-8]

$$ROOH + M^n \longrightarrow RO\cdot + HOM^{n+1}$$

$$ROOH + M^{n+1} \longrightarrow ROO\cdot + H^{\oplus} + M^n$$

The rates of these reactions depend strongly on the kind of metal-ion complexes present: Fe or Cu phthalocyanine complexes are extremely effective catalysts for peroxide decomposition; FeEDTA is usually inert. In water Fe^{2+} is oxidized rapidly by ROOH, but Fe^{3+} is often nearly inert. In high-pH, aquatic systems where Fe is largely hydrated and insolubilized, its participation in electron transfer reactions may be minimal, but in acidic water Fe or Cu ions could be important in oxidation.

Natural Retarders

A wide variety of natural products can retard or inhibit radical oxidation processes. For example, flavin constituents of pigments (such as quercitol) have phenolic-OH groups

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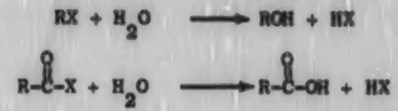
[*] Oxygen quenching may reduce the efficiency of the process in the environment.[4]

which are very reactive in H-atom transfer to peroxy or alkoxy radicals. In many natural eutrophic waters, the steady-state concentration of inhibitors or retarders present regulates the concentration of RO· or RO_2· radicals through termination (conversion to unreactive radicals). Very likely numerous carotenoid-like molecules are also present that can function as efficient quenchers of $^1O_2$.[9]

Hydrolysis

Hydrolysis of organic molecules usually results in introduction of a hydroxyl function (-OH) into a substrate, most commonly with the loss of a leaving group (-X). These reactions



$$RX + H_2O \longrightarrow ROH + HX$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}X + H_2O \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + HX$$

may be catalyzed by acids (k_A) or bases (k_B) or both. The kinetics of hydrolysis of a substrate can be expressed as

$$-\frac{ds}{dt} = R_{hyd} = k_{obs}[S] = k_B[OH^-][S] + k_A[S][H^+] + k_N'[H_2O][S] \qquad (9)$$

The last term is the neutral reaction with water, and in an aqueous environment $k_N'[H_2O]$ is constant ($= k_N$). With few exceptions hydrolysis reactions are usually first order in substrate. Equation (9) can then be simplified to

$$k_{obs} = k_B[OH^-] + k_A[H^+] + k_N \qquad (10)$$

From the integrated form of equation (9), the half-life for hydrolysis of the substrate, $t_{\frac{1}{2}}$, is calculated.

$$t_{\frac{1}{2}} = \frac{0.693}{k_{obs}} \qquad (11)$$

From equations (10) and (11) it is clear that the half-life will be dependent on the pH when k_B and/or $k_A \neq 0$. From the autoprotolysis water equilibrium,

$$[H^+][OH^-] = K_w \simeq 10^{-14} \qquad (12)$$

equation (10) may be rewritten

$$k_{obs} = \frac{k_B\ K_w}{[H^+]} + k_A\ [H^+] + k_N \qquad (13)$$

The contribution of each term to k_{obs} will depend on the acidity (or pH) of the solution; three regions may be defined:[10]

Acid $$k_A[H^+] > k_N + \frac{k_B K_W}{[H^+]} \quad , \quad \log k_{obs} = \log k_A + \log[H^+] \qquad (14)$$

$$= \log k_A - pH$$

Base $$\frac{k_B\ K_W}{[H^+]} > k_N + k_A[H^+] \quad , \quad \log k_{obs} = \log k_B K_W - \log [H^+] \qquad (15)$$

$$\log k_B K_W + pH$$

Neutral $$k_N > k_A[H^+] + \frac{k_B K_W}{[H^+]} \quad , \quad \log k_{obs} = \log k_N \qquad (16)$$

These expressions implicitly assume that the catalyzed processes are first order in acid $[H^+]$ or base $[OH^-]$ concentration. Such behavior is almost always the case in the range of pH 2 to 12 and frequently extends to greater extremes.

From the above discussion it is seen that the observed rate of hydrolysis depends on the relative values of k_N, k_B, and k_A. Within a class of compounds the individual rate constants may vary by several orders of magnitude with the structure and substitution on the molecule. When the acid and base catalyzed mechanisms are operative, the observed rate will also be pH dependent. The hydrolysis rates of carboxylic amides and esters are typically described by acid and base catalyzed mechanisms in their respective regions with a distinct minimum between pH 4 to 7, which indicates no contribution from k_N. Some carbamates are hydrolyzed by all three mechanisms, showing a pH independent rate from pH of about 3 to 7 or 8, with the respective acid and base catalyzed mechanisms being important in the outlying pH regions.[11] For many alkyl halides no acid catalyzed mechanism is found, and the hydrolysis rate is pH independent to beyond pH 10 where the base reaction becomes important.[12] Thus, while each class of compounds possesses different reactivity toward hydrolysis, the reaction rates can be expressed in a common analysis that can be used for environmental assessments.

The dependence of the hydrolysis rate on the pH of the solution is conveniently depicted by a plot of log k_{obs} as a function of pH.[10b] From expressions (14), (15), and (16), it is seen that in the pH range where the base catalyzed process is dominant, a slope of +1 is found; a slope of -1 is found in the acid catalyzed region. The neutral hydrolysis is pH independent and shows a slope of zero.

Present knowledge of the theoretical and experimental aspects of hydrolysis reactions makes laboratory studies of hydrolysis rates useful for environmental estimates. Precaution must be taken, however, to ensure that experimental artifacts are not introduced into the kinetic data. The use of buffer salts to maintain a constant pH is a common and acceptable practice, but appropriate experiments should be carried out to demonstrate the absence of any effects of buffer catalysis or ionic strength. Another problem may arise in the use of organic cosolvents to increase the solubility of the organic substrate in the aqueous solution. Although this practice does expedite the experimental procedures, it can change the rate constant considerably over that found when water is the sole solvent.

For some organic compounds, environmental hydrolysis rates can be estimated from the extensive body of published data not originally intended for environmental relevance. The principal limitations of such data are the frequent use of elevated temperatures and mixed organic-water solvent systems. These conditions can often be corrected for by using the empirical data treatment relationships developed by physical organic chemists in their studies of mechanisms and kinetics of chemical reactions. Although few studies have been carried out at concentrations in the ppm range, the hydrolysis reaction is usually first order in pollutant and the half-life estimates are then not concentration dependent (equations 10 and 11). Half-life estimates for several organic halides and epoxides calculated from literature data are listed in Table 3 and can be quite informative for assessing degradation by hydrolysis processes.[12]

Table 3

HALF-LIVES FOR SELECTED ORGANIC HALIDES AND EPOXIDES TOWARD HYDROLYSIS AS A FUNCTION OF pH AT 25°C IN WATER

Compound	pH 4	pH 7	pH 10
Methyl bromide	480 hr →	same →	same
Methyl chloride	10^4 hr →	same →	same
Isopropyl bromide	50 hr →	same →	same
Isopropyl chloride	940 hr →	same →	same
Allyl chloride	166 hr →	same →	same
Benzyl chloride	15 hr →	same →	same
Chloroform	32000 yr	3500 yr	3.5 yr
Isobutylene oxide	0.3 hr	106 hr	175 hr
Epichlorohydrin	181 hr	197 hr	197 hr
1,3-Cyclohexadieneoxide	0.42 hr	6 min	53 min

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PREDICTION OF VOLATILIZATION RATE OF POLLUTANTS IN AQUEOUS SYSTEMS

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Introduction

For some pollutants volatilization is a significant mechanism of loss from water bodies thus the prediction of the rate of this process is necessary.

Figure 1 gives a diagramatic representation of this and other processes which may occur. Although the discussion here is primarily about volatilization, the equations developed also apply to the reverse process of direct absorption from the atmosphere.

The rate of volatilization can be expressed by an equation of the form

Mass flux	=	Mass Transfer Coefficient	x	Concentration Driving Force
N (mol/m^2s)		K (m/s)		ΔC (mol/m^3)

It is suggested that the fundamentally different terms K and ΔC must be considered and quantified separately. The mass transfer term contains kinetic or transport rate information and depends on the local fluid turbulence regime whereas the concentration term is essentially thermodynamic in nature. A knowledge of both is essential. The approach taken here is to review the structure of the flux equation, identify the critical parameters which control K and ΔC, discuss each in turn outlining the present state of knowledge and suggesting methods by which the appropriate data can be determined with a view to using the equation for predictive purposes. Finally, some complications are discussed.

Mass Flux Equation

Diffusion in a single phase is quantified by Fick's Law containing a molecular or eddy diffusivity. In two-phase systems this law may be applied twice and equilibrium assumed at the interface leading to the Whitman two-film theory. This has recently been extensively applied by Liss (1974) to environmental conditions.

The flux equation takes two forms which are mathematically identical, the preferred equation depending on which film controls the mass transfer by offering the greater resistance.

$$N = K_{OL}(C-P/H) \quad \text{where} \quad 1/K_{OL} = 1/K_L + 1/(HK_G/RT)$$

or

$$N = K_{OG}(HC-P)/RT \quad \text{where} \quad 1/K_{OG} = 1/K_G + H/RT\,K_L$$

where the subscripts on the mass transfer coefficients (K) define them as liquid film (L), vapor film (G), overall liquid (OL) or overall vapor (OG), C is the pollutant concentration in the liquid (mol/m^3), P is its partial pressure in the atmosphere (atm) and H is the Henry's Law constant ($atm/(mol/m^3)$) defining the equilibrium by the equation $P = HC$. In most cases one film dominates. Transfer of water soluble pollutants, such as SO_2 (which have high values of H) tend to be gas film controlled whereas less soluble pollutants such as chlorinated hydrocarbons (which have low values of H) tend to be liquid film controlled. It is assumed here that the terms C and P are determined experimentally or alternatively one of them is the object of the modelling exercise. Fortunately, for most pollutants, P is negligible, notable exceptions being some airborne compounds such as sulphur and nitrogen oxides in which ambient levels may be calculated by an appropriate dispersion equation. The ability to calculate the flux N thus depends fundamentally on a knowledge of the three terms, H, K_G and K_L. These are discussed separately below.

H - The Henry's Law Constant

Henry's Law constant data are readily and reliably available for the common gases and for most reasonably soluble liquids as a function of temperature and often as a function of the concentration of other materials such as electrolytes in aqueous solution. Unfortunately, for certain compounds of environmental interest such as chlorinated hydrocarbons H data are less available and reliable. Thermodynamically, H is an expression of the relative activity of the pollutant in the vapour and liquid phases. Equating the chemical potential or fugacity of the pollutant in each phase leads to an equilibrium equation using the Raoult's Law convention

$$x \gamma P^S = \phi y P_T$$

where x and y are the mol fractions in the liquid, and vapor respectively, γ, the liquid activity coefficient, ϕ, the vapor fugacity coefficient, P^S, the saturation vapor pressure of the liquid pollutant at the ambient temperature and P_T, the total atmospheric pressure. Fortunately, for most compounds which do not chemically associate in the vapor, ϕ is unity at all environmental pressures. It can be shown that for aqueous systems H is equivalent to $18 \times 10^{-6} \gamma P^S$ atm/(mol/m^3). Assuming that experimental data for H is not available, it can be estimated from other thermodynamic data although different treatments are required depending on the phase state of the pollutant (Mackay and Shiu, 1975).

There is a tendency to believe that substances which have very low vapor pressures (P^S) will tend to have low Henry's Law constants (H), will therefore be strongly partitioned into the liquid with evaporation then being unimportant. This is certainly true for many compounds, especially ionic species. However, for high molecular weight hydrophobic substances, the low value of P^S is offset by the high activity coefficient γ. This gives a higher Henry's Law constant than is first suspected. Evaporation can therefore be very significant. In addition, although the concentration of these substances is usually low in water bodies even a very low mass flux can have a profound effect on the environmental concentration, significantly depleting the aqueous phase of the contaminant. This was first observed by workers such as Acree et al (1963) in handling solutions of DDT and has been discussed by Mackay and Wolkoff (1973) and Mackay and Leinonen (1975). Coincidentally, these hydrophobic substances may tend to be biologically active because of their preferred partition into lipid phases. The major difficulty in predicting evaporation rates occurs for substances such as poly nuclear aromatics, chlorinated hydrocarbons, or organometallic compounds. These substances have very low vapor pressures (P^S) and the data, when available, may be unrealiable and probably exist only for the solid state. They also have high activity coefficients (γ) as evidenced by their low aqueous solubility. The measurement of these low solubilities requires extreme care. It is suggested here that it is better and easier to measure the group γP^S and hence H directly by measuring an evaporation rate under controlled conditions. This has been done recently by Dilling et al (1975) in a discussion of evaporation and reaction rates of chlorinated hydrocarbons from water. Their technique involved exposing a stirred beaker of pollutant solution to the atmosphere and following the concentration decrease. Unfortunately, such measurements give a mass flux which is dependent on the mass transfer coefficient and cannot therefore be used to determine H accurately. A preferable system is to expose the evaporated solution under conditions where the flux rate is independent of the mass transfer coefficient, i.e., the vapor in contact with the liquid is always close to equilibrium. The mass flux rate is then dependent only on the amount of vapor contacted with the liquid and not the exposure conditions. Such an apparatus is shown in Figure 2 in which an air stream is sparged into a liquid. It is believed that the exit vapor achieves > 95% equilibrium with the well stirred liquid. The concentration of the pollutant in the liquid is then monitored as a function of time and the slope of the concentration time curve gives the Henry's Law constant directly. An alternative approach described by Mackay, Shiu and Wolkoff (1975), is to contact a liquid with successive volumes of vapor, extract the pollutant into the vapor and measure the vapor concentration of the pollutant. This vapor phase equilibration approach first proposed by McAuliffe (1971), is applicable only to relatively volatile pollutants of low aqueous solubility.

The environmental contaminants of greatest concern tend to be those which are present in very low concentrations and unfortunately this renders experimental work more difficult due to adsorption on solid surfaces, interference by other substances such as electrolytes and humic acids, the presence of surface active materials, particulate matter and the presence of material in colloidal or micelle form. These difficulties combine to make concentration measurement difficult in laboratory conditions and exceptionally difficult in environmental conditions. There is thus a strong case for obtaining H data from the actual environmental water being studied using a system as described earlier.

K_G the Vapor Phase Mass Transfer Coefficient

Under environmental conditions K_G is of the order of 1 cm/s. Fortunately, there is a considerable body of experience about K_G as a function of wind speed, atmospheric turbulence, and temperature profile and hence on the diurnal variation. Many of these data come from studies of water evaporation. There is a poor understanding of the effect of waves on K_G especially under rough conditions. Ironically, it is under these conditions that fluxes tend to be highest and therefore, quantification of flux rate is probably most important. Experimental measurement is easiest under stagnant or calm conditions when the fluxes are lowest and possibly then of less importance. Actual flux rates under environmental conditions can be measured for some substances for which the resistance lies in the vapor phase by sampling the atmosphere at two levels. This has been done recently for sulphur dioxide absorption into lakes and onto snow surfaces. K_G can also be estimated for a particular environmental situation by evaporating a liquid of known volatility (Mackay and Matsugu 1973).

It must be noted that for many low solubility pollutants the liquid phase controls and the structure of the flux equation renders the flux rate very insensitive to the value of K_G assumed, thus a high degree of accuracy is unnecessary.

K_L the Liquid Phase Mass Transfer Coefficient

There is considerably less understanding of the values of and variations in K_L. Reported values range from 10^{-2} to 10^{-4} cm/s with a typical value of 10^{-3} cm/s or one thousandth of the vapor phase values. The coefficient is very sensitive to the fluid state of the water especially the level of turbulence and the presence of waves. It depends on the surface properties of the solution, on the wind speed and the turbulence below the surface and on the depth of the water body, which may be a river, lake or ocean. A common (and unfortunate) practice is to calculate an equivalent stagnant diffusion layer thickness obtained by dividing the molecular diffusivity (typically 10^{-5} cm^2/s) by the mass transfer coefficient thus giving typical values of 0.01 cm or 100 microns. In reality it is likely that eddy diffusion controls the flux except very close to the surface where the mechanism may be unsteady state molecular diffusion into elements of liquid which are periodically moved to and from the surface by hydrodynamic or surface instabilities. The nature of this process is only poorly understood because of the difficulties of measuring and observing them. Again the conditions of greatest interest are those when the fluxes are high, i.e., the water will be turbulent and thus experimentally most difficult and when laboratory conditions are most inapplicable. Some recent measurements of liquid phase transfer coefficients have been reviewed by Weiler (1974).

There has been considerable work on oxygen transfer relating to river aeration and on CO_2 transfer. It is probably essential to measure actual transfer rates in situ, because laboratory techniques are unlikely to simulate environmental conditions adequately. Unfortunately, in situ measurements are extremely difficult although radon diffusion measurements have been used for ocean transfer by Broecker (1971). We have recently used hydrocarbons for this purpose in the laboratory although in the environment experimental difficulties are introduced by the presence of fast horizontal diffusion and which would force the use of a system to artificially limit horizontal diffusion by some form of corral. The simplest laboratory procedure for measuring K_L is to follow the volatilization of an hydrocarbon from aqueous solution as shown in Figure 3 for a wind-water tank. The slope of the concentration-time curve gives K_L directly. Another approach which we are currently investigating is to measure the dynamic temperature profiles in the upper layers of a water body and from the calculated heat flux deduce the mass flux by analogy between thermal and mass diffusion.

The major areas of inadequate understanding are the dependence of K_L on wind speed, the presence of waves, and on the molecular weight of the pollutant. This latter effect is particularly important when using data for radon or oxygen diffusion to predict flux rates for high molecular weight substances such as PCB^s. There is a real need for a simple method of *in situ* K_L measurement.

SOME COMPLICATIONS

Most environmental water bodies are covered by a surface microlayer which contains protein material, hydrophobic substances, and surface active agents (Andren et al 1975), which retard mass transfer to some extent and concentrate some pollutants. Most experimental work on microlayers use artificial cetyl alcohol films which may behave quite differently from environmental layers. The effect of these layers is poorly understood.

In quantifying evaporation rates it may be necessary to include terms for the rate associated with bursting bubbles particularly under rough conditions. Direct entrainment of spray particles into the atmosphere is particularly important for transport of ionic compounds. The reverse process of direct deposition can also be quantified by these equations, however, the situation is complicated by the contribution of absorption during rain and snowfall and adsorption of the pollutant on particulate matter which may also settle on to the water body.

Another difficulty arises when the pollutant is present in colloidal or micelle form rather than as a true solution or when it is adsorbed on particulate matter or where other substances such as electrolytes or humic acids influence the activity coefficient and thus H. Many of these contaminants tend to be concentrated in the surface organic microlayer where the immediate chemical environment and hence the physical and equilibrium properties are not well understood.

CONCLUSIONS

For a particular pollutant the prediction of the volatilization rates requires (i) a knowledge of the pollutant concentration in the water body (C) and confidence that it is in true solution and not significantly modified by the presence of other contaminants, (ii) a knowledge of the atmospheric concentration P and (iii) Henry's Law constant data (either literature values or experimentally measured values preferably from laboratory evaporation systems or from estimated solubility and vapour pressure data.) Approximate values of the transfer coefficients K_L and K_G can be obtained and used to estimate the mass flux rate, which will probably be accurate within a factor of about five. This may be sufficient to demonstrate that for a specific pollutant, evaporation is not a major pathway. If it is significant, then accurate determination of the volatilization rate depends on having reliable Henry's Law constant data, reliable mass transfer coefficient data, preferably determined *in situ*. In most cases the critical quantity is K_L with the value of K_G being required only approximately because the resistance lies mainly in the liquid phase. The two phase resistances are equal when $H = K_L RT/K_G$. K_G data can be obtained from evaporation rate measurements but K_L measurement

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and prediction presents a more difficult problem. The inability to predict K_L accurately for a given environmental situation and lack of understanding of the effects of surface microlayer and particulate and dissolved organics on the liquid phase activity represent the most significant gaps in current capability to predict environmental volatilization rates

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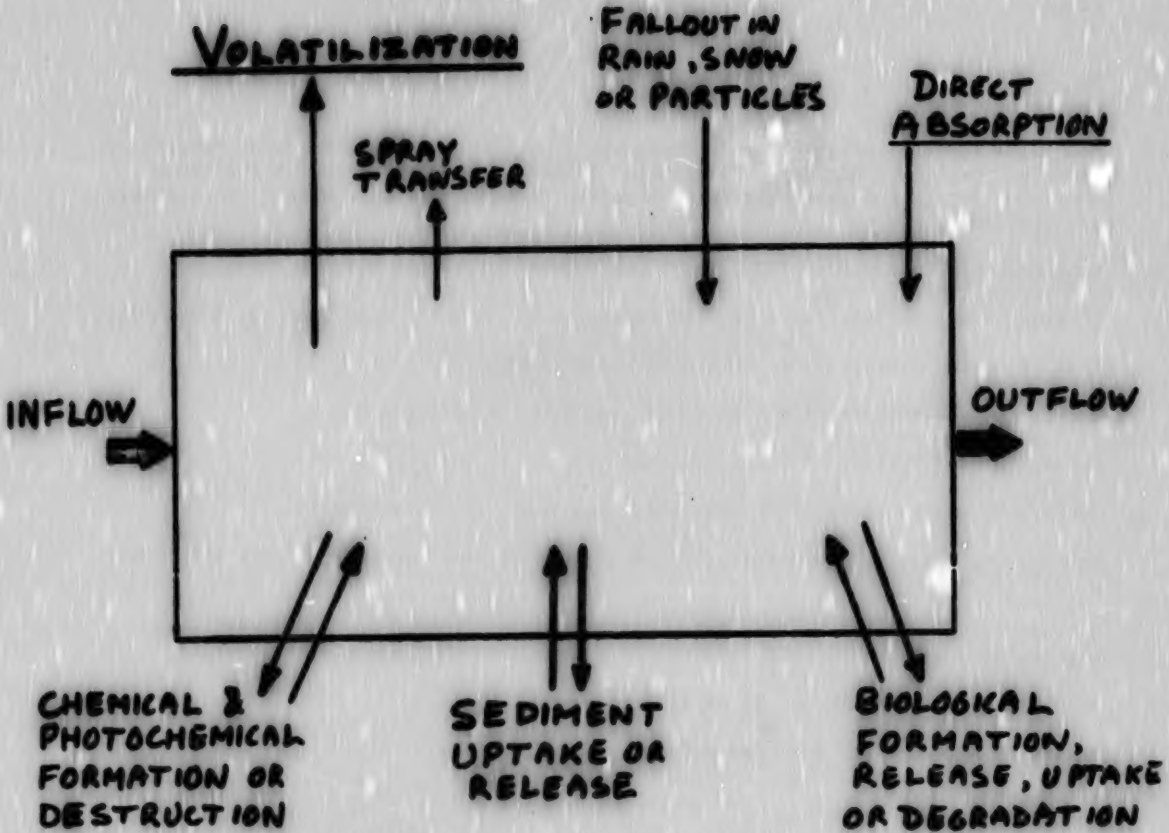

VOLATILIZATION
SPRAY TRANSFER
FALLOUT IN RAIN, SNOW OR PARTICLES
DIRECT ABSORPTION
INFLOW
OUTFLOW
CHEMICAL & PHOTOCHEMICAL FORMATION OR DESTRUCTION
SEDIMENT UPTAKE OR RELEASE
BIOLOGICAL FORMATION, RELEASE, UPTAKE OR DEGRADATION

FIGURE 1

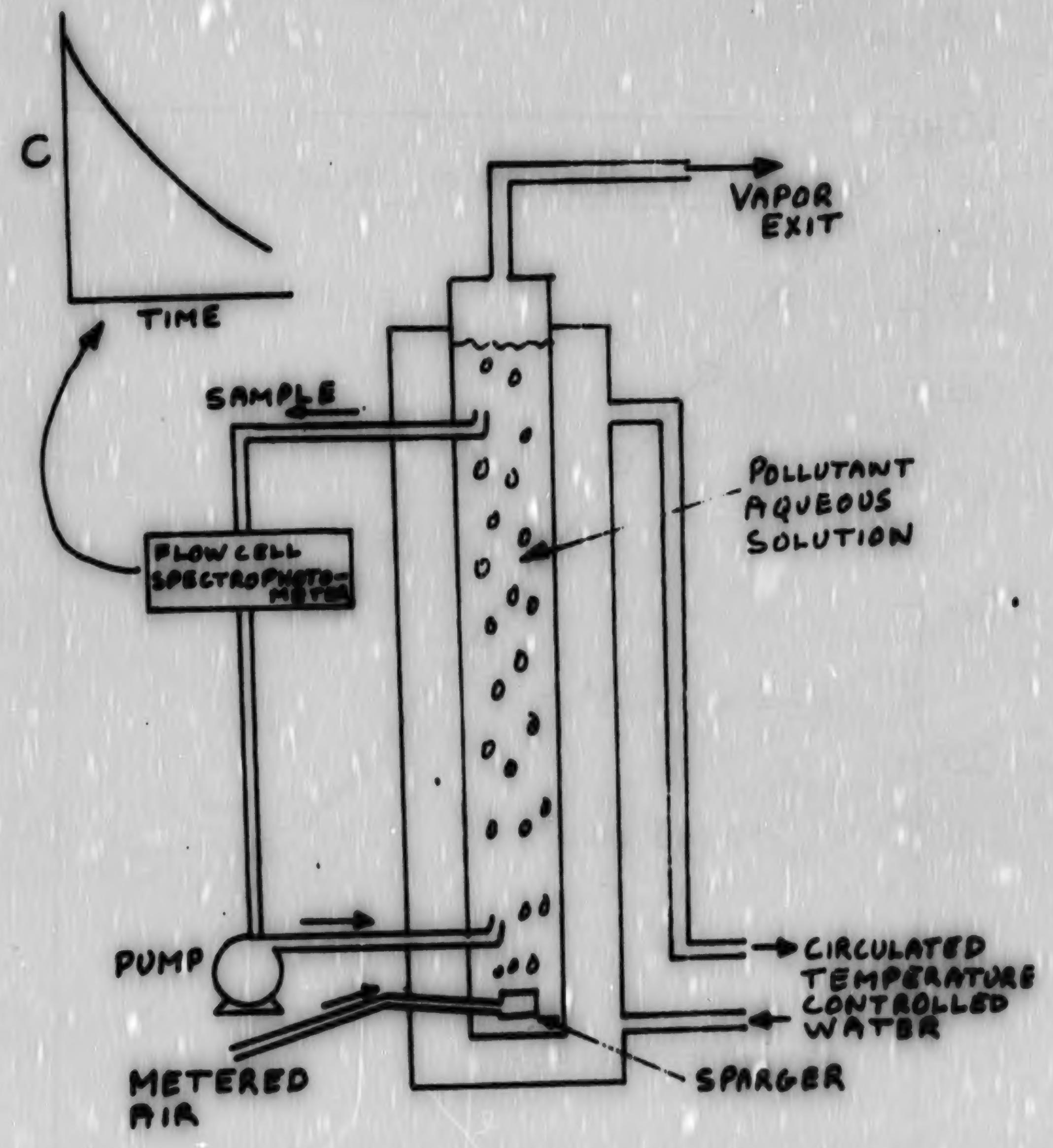
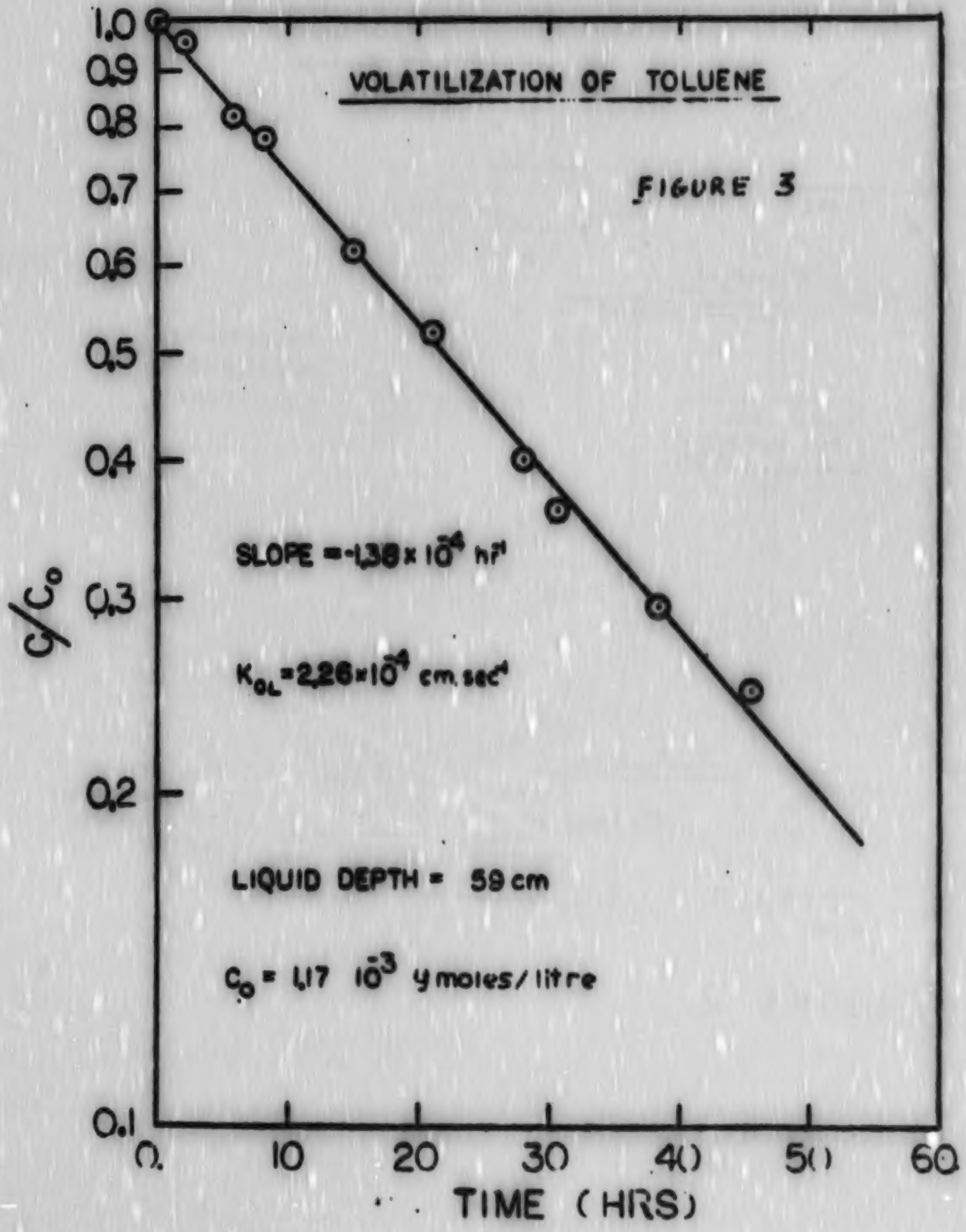

C
TIME
VAPOR EXIT
SAMPLE
POLLUTANT AQUEOUS SOLUTION
FLOW CELL SPECTROPHOTOMETER
PUMP
CIRCULATED TEMPERATURE CONTROLLED WATER
METERED AIR
SPARGER

FIGURE 2



VOLATILIZATION OF TOLUENE

FIGURE 3

SLOPE = -1.38×10^{-4} hr^{-1}

$K_{OL} = 2.26 \times 10^{-4}$ cm. sec^{-1}

LIQUID DEPTH = 59 cm

$C_0 = 1.17\ 10^{-3}$ g moles/litre

COMPLEXATION, PRECIPITATION AND ADSORPTION OF TRACE METALS IN WATER

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Introduction

Metals introduced into fresh water or marine environments in dissolved forms are partially removed to the sediments by precipitation, adsorption onto mineral or organic particles, and incorporation into biological material. Particulate metal inputs may be partially dissolved or desorbed in their travel to the sediments. In fresh water systems, a fraction of each input metal leaves the system in dissolved outflow. This fraction depends upon factors affecting the completeness of adsorption, precipitation, and sedimentation of each metal. Schindler(1975) has proposed a chemical approach, based on adsorption to oxide surfaces, e.g., SiO_2, to predict the relative residence times of metals in lakes and the absolute residence times in seawater. Among the important physical-chemical factors affecting the driving forces of metal sedimentation via adsorption and precipitation are: (1) pH (acid-base equilibria); (2) complexation of metals by ligands, with the possibility of competition between metals for limited amounts of complexing ligand (Morel, McDuff, and Morgan (1973); Morel and Morgan (1972); Stumm and Morgan (1970); (3) pε (redox processes, affecting relative abundances of potential precipitating ligands such as sulfide and oxidation states of metals, e.g., Fe(III) vs. Fe(II)); (4) area of adsorptive surfaces in relation to volume of solution phase; (5) ionic strength, affecting solubilities of pure solid phases and the adsorption tendencies of trace metals on surfaces; (6) temperature.

The strong influence of pH on solubility, adsorption, complexation, and redox equilibria is well recognized. It is necessary to be aware that significant temporal and spatial variation in pH take place in natural water systems, and may account for important alterations in trace metal speciation patterns (Schindler, 1975; Morel, McDuff, and Morgan, 1973).

Complexation by inorganic ligands tends to increase the residence time of metals in natural water systems by impeding adsorption (MacNaughton and James, 1974; MacNaughton, 1973; Schindler, 1975; Vuceta, 1976) or preventing precipitation (Stumm and Morgan, 1970). Metals initially in particulate forms may be "mobilized" (dissolved, desorbed) by complexation or pH alteration, or both.

Thus, it is necessary to consider simultaneously the influences of a number of chemical processes in order to predict the forms, transport, residence time, and fates of trace metals in natural water systems (water and sediments). Needed computational tools are available to describe acid-base, complex formation, solubility, and redox equilibria for model systems of considerable complexity (Morel and Morgan, 1972; McDuff, Morel, and Morgan, 1973; McDuff and Morel, 1973).

Adsorption equilibria for trace metals have been described mathematically by a number of investigators. Extensive reviews and comparisons have been provided by MacNaughton (1973, 1974); Parks (1975); James, Stiglich and Healy (1975); and Vuceta (1976). In the present work we wish to describe interaction of metal adsorption equilibria with acid-base, solubility, complexation, and redox equilibria. We report computations for a number of model systems in which these equilibria interact. We make use of two basically different adsorption models to illustrate expected patterns, (a) an adsorption-hydrolysis, ion-solvent interaction model (AHIS) proposed by James and Healy (1972); (b) a surface complex formation model (SCF) proposed recently by Schindler, Fürst, Dick, and Wolf (1975) for the SiO_2 surface and Hohl and Stumm (1975) for the Al_2O_3 surface, representing a further development of earlier models variously referred to as "ion-exchange," "specific chemical interaction," and "specific adsorption" models. Both the AHIS and SCF models have been found capable of mathematically fitting experimental results on adsorption of metals to certain oxide surfaces as a function of pH and variations in specific ligands (MacNaughton, 1974; James, Stiglich and Healy, 1975; Vuceta, 1976). Important questions remain to be settled with respect to the fundamental merits of these models as *predictive* tools.

Adsorption Models

Adsorption of metals from aqueous solutions onto oxide surfaces has been described theoretically in terms of two concepts: (i) electrostatic influences on the distribution of charged species in the vicinity of a charged interface; (ii) specific binding of metal ion species with functional groups on the surface. Electrostatic models include simple charge-dependent ion exchange in the diffuse double layer or the Stern layer (Parks, 1975). Chemical interaction models postulate bond formation to sites on the surface of the solid, i.e., the inner coordination sphere of the adsorbing metal interacts with a ligand on the surface. In a sense, we might characterize the models proposed for metal (or anion) adsorption as either *electrostatic* models with chemical "corrections," or *chemical* models with electrostatic "corrections." For hydrolysable metal ions, which are *bound to the* protonated hydroxyl ligand in solution, it seems reasonable to expect that these same metals would be bound by similar ligands on the surface of hydrated oxides.

The AHIS model of James and Healy (1972) postulates the adsorption of free and hydrolysed metal ion species, each with its own free energy of adsorption, resolved into coulombic, solvation, and chemical components:

$$\Delta G_{ads,i} = \Delta G_{coul,i} + \Delta G_{solv,i} + \Delta G_{chem} \qquad (1)$$

with

$$\Delta G_{coul,i} = Z_i F \Psi_o \qquad (2)$$

and $\Delta G_{solv,i}$ depends upon: Z_i ; the hydrated radius of the adsorbing ion; the ionic radius; and the dielectric constants of the bulk solution, the interfacial region, and the solid. ΔG_{chem} is assigned the *same* value for *each* metal ion species. Adsorption is described by a Langmuir isotherm, in which the equilibrium constant for each metal ion species is

$$K_{ads,i} = \exp(-\Delta G_{ads,i}/RT) \qquad (3)$$

and the maximum adsorption density is fixed by the hydrated radius of the metal ion. Total adsorption density of the metal, $\Sigma \Gamma_i$, is determined by summing over the individually-computed densities for each species. ΔG_{chem} is a fitting parameter in most applications of the model (MacNaughton, 1974); it has been measured directly in certain cases. From a conceptual point of view, the status of ΔG_{chem} in relation to $\Delta G_{solv,i}$ is not obvious. As pointed out by James, Stiglich and Healy (1975), the James-Healy model describes a "physical adsorption" processes. Yet, adsorption of a species such as $Cu(OH)_2(aq)$ would necessarily involve chemical forces since ΔG_{coul} and ΔG_{solv} would be zero. Similarly, the demonstrated adsorption of *any* species at $\Psi_o = 0$ demands *chemical* interaction.

The SCF model for metal ion binding to hydrous oxide employs a framework similar to that developed by Tanford (1961) to describe binding of metal ions to macromolecules with identical protolysable monomer groups. *Intrinsic* acid dissociation equilibrium constants and *intrinsic* metal binding equilibrium constants are defined in the absence of electrostatic effects, and corresponding *apparent* constants are obtained under specified pH conditions by applying an electrostatic correction function. For the case of the hydrated SiO_2 *surface,* two types of equilibria are described:

$$\equiv SiOH = \equiv SiO^- + H^+, \; K_{a,intr} \qquad (4)$$

and

$$m \equiv SiOH + M^{z+} = (\equiv SiO)_m M^{z-m} + mH^+, \; {}^*\beta^s_{m,intr} \qquad (5)$$

The corresponding apparent constants are obtained as

$$k_{a,app} = K_{a,intr}\, e^{z\Psi_o/RT} \qquad (6)$$

$$^*\beta^s_{m,app} = {^*\beta^s_{m,intr}}\, e^{(z-m)\Psi_o/RT} \qquad (7)$$

Note the major role played by pH in both the AHIS and SCF models, affecting the adsorption process through Ψ_o and through hydrolytic equilibria in solution. In the SCF model, hydrogen ions are directly involved in the acid dissociation equilibrium of the binding ligand silanol groups of the surface. For earlier development of SCF-like models see Dugger, et al. (1964) and Stumm, Huang and Jenkins (1970). Recently, Yates, Levine and Healy (1974) put forward a site-binding model of the electrical double layer at the oxide/water interface which introduces formation constants for interfacial ion pairs between $\equiv MO^-$ groups and monovalent cations and includes quantitative consideration of the acid-base behavior of $\equiv MOH_2^+$, $\equiv MOH$, and $\equiv MO^-$ entities on the surface. Such a site-binding model is equivalent to the SCF model (compare equations (4) and (5), above).

Some difficulties in quantitative applications of an SCF model to prediction of behavior in complex systems relate to: (i) questions concerning the functions $\exp(z\Psi_o/RT)$ and $\exp(z-m)\Psi_o/RT)$ for obtaining apparent constants; more experimental detail is needed for different ionic strengths, over a pH range from 5 to 9, (ii) questions concerning the independent adsorption of anions, such as sulfate and phosphates in natural systems, and consequent effects on surface charge and potential.

Solution Composition and Adsorption

Adsorption of metals onto surfaces can be viewed as competition between two or more ligands for a fixed total concentration of metal. The distribution coefficient is one way of describing the result of the competition:

$$D = \frac{\text{total surface concentration of metal}}{\text{total concentration of aqueous metal}} = \frac{M_s}{M_{aq}} \qquad (8)$$

Let us examine it in terms of the SCF model. From equations (5) and (7)

$$\frac{\{(\equiv SiO)_m M^{z-m}\}}{\{\equiv SiOH\}^m} \cdot \frac{[H^+]^m}{[M^z]} = {^*\beta^s_{m,app}} \qquad (9)$$

where { } represents surface concentration of metal complex. For protonated ligands HL_j in the aqueous phase (Schindler, 1975),

$$M_{aq} = [M^z]\,(1 + \sum^{j}\sum^{n} {^*\beta_{jn}}[HL_j]^n\,[H^+]^{-n}) \qquad (10)$$

Thus,

$$D = \frac{M_s}{M_{aq}} = \frac{\sum^{m} \{\equiv SiOH\}^m [H^+]^{-m}\, {^*\beta^s_{m,app}}}{1 + \sum^{j}\sum^{n} {^*\beta_{jn}}\,[HL_j]^n\,[H^+]^{-n}} \qquad (11)$$

The surface concentration of $\equiv SiOH$ groups depends in turn upon the pH and $pK_{a,app}$ of the acid dissociation. Thus

$$\{SiOH\} = \frac{C^s\,[H^+]}{[H^+] + K_{a,app}} \qquad (12)$$

where C^s is the concentration of unbound (free) surface OH groups.

The quantity of C^s (e.g., moles of groups per unit weight of solid) describes the concentration of unbound surface ligands; C^s_o, the total concentration of surface ligands, is an experimentally determinable quantity through titration procedures (Schindler, Fürst, Dick and Wolf, 1975; Hohl and Stumm, 1975). Thus, C^s_o, $K_{a,app}$, and the $^*\beta^s_m$ values are the important properties of the particulate material. The presence of complexing ligands in the aqueous solution, here formally represented as HL_j (e.g., H_2O, HCO_3^-, organic acids, sulfate, chloride, etc.) increases M_{aq} at the expense of M_s, i.e., the distribution coefficient is lowered. The strong influence of pH is evident in equations (11) and (12). Increasing pH can either increase or decrease adsorption in given pH ranges. The net effect depends upon the magnitude of the equilibrium constants for metal-surface binding and aqueous complexation (including especially hydrolysis), and upon the relative stoichiometrics of surface and aqueous ligands. As reported by MacNaughton and James (1974), aqueous chloro complexes of Hg(II) compete with adsorption to oxide surfaces. Similar distribution coefficients can be constructed for an AHIS model. However, the influence of pH is not as explicitly seen in the AHIS model.

Mixed Ligand Complex Adsorption: Formally, the AHIS model appears as a mixed ligand complex model, if one recognizes that $M(OH)_n$ species are imagined to be bound to the surface by a chemical force (ΔG_{chem}). Additional definitions of ΔG_{chem} for adsorption of such species as ML(aq) or $M(OH)_n L(aq)$ are required to specify adsorption possibilities in media containing complex species other than hydrolysis products. We model non-adsorbable complexes, e.g., CuCITRATE, by imposing large, positive ΔG_{chem} for all such complexes. Favorable ΔG_{chem} values might also be imposed to account for observed enhanced adsorption of certain metals in the presence of specific complexing agents (MacNaughton, 1973).

The SCF models do not describe mixed ligand complexes, i.e., free metal is bound to surface ligands. Such processes as $M\ L + \equiv SOH = (\equiv SO)M(L) + H^+$ can, however, be envisioned. Experimental data to identify patterns of such possible reactions are not yet available (but again, see MacNaughton, 1973, for some examples).

Illustrative Example Comparing AHIS and SCF Models

Two models were applied to a simple 3-metal (Na^+, Cu^{2+}, H^+), 2-ligand (Cl^-, OH^-), and one oxide (α-SiO_2) system at 25°C and ionic strength 1×10^{-3}M. For detailed results, see Vuceta (1976).

The AHIS model employed ΔG_{chem} of -3.0 kcal mole^{-1} for Na^+ and - 8.0 kcal mole^{-1} for all Cu^{2+} species. The ZPC pH for SiO_2 was taken at 2.0, ϵ_{solid} at 4.3. The system surface area was 50 m^2/ℓ (corresponding in the SCF model to 2.24×10^{-4} moles of silanol groups per liter). Total Cu(II) in the system was 1×10^{-6}M. For the SCF model we chose (on the basis of experimental data describing adsorption densities vs. pH) the following apparent surface complex formation constants: $\log {}^*\beta^s_{1,Cu} = -1.8$ and $\log {}^*\beta^s_{2,Cu} = -3.8$ (mole/liter scale for the system of fixed solid-surface concentrations); $\log {}^*\beta^s_{1,Na} = -4.2$. At pH 7.0, the following results were obtained:

AHIS	Surface					Aqueous	
Species:	Cu^{2+}	$CuOH^+$	$Cu(OH)_2$	$Cu(OH)_3^-$	$Cu_2(OH)_2^{2+}$	Cu^{2+}	$Cu(OH)_2$
-log molar:	7.78	6.21	6.46	17.9	12.3	8.27	7.95

$$D^* \cong \frac{10^{-6.21} + 10^{-6.46} + 10^{-7.78}}{10^{-8.27} + 10^{-7.95}} = 59$$

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SCF	Surface		Aqueous	
Species:	Cu(SiO)	$Cu(SiO)_2$	Cu^{2+}	$Cu(OH)_2$
-log molar:	7.16	6.04	8.49	8.23

$$D^* \cong \frac{10^{-7.16} + 10^{-6.04}}{10^{-8.49} + 10^{-8.23}} = 108$$

Note: ~ 60% of total SiOH groups in H^+ form; 39% in Na^+ form; 1% in Cu^{2+} form.

Models for Multi-metal, Multi-ligand Systems with Adsorption

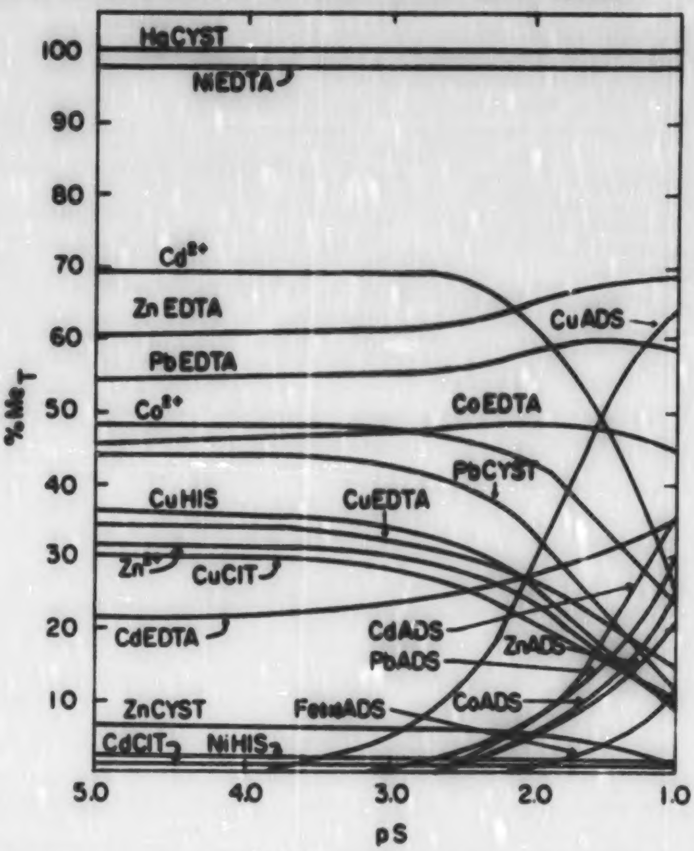
Previous Work: Schindler (1975) has developed SCF models for distribution coefficients of Zn(II) and Cu(II) in fresh water systems (lakes, rivers) in which SiO_2 and TiO_2 are used as model sediments. He has also predicted residence times of 9 elements in the ocean based on SCF models. Agreement with observed data was reasonable in a majority of cases. Guy, Chakrabarti, and Schramm (1975) constructed a laboratory experimental model for Cu(II), Cd(II), and Zn(II), with MnO_2, clay, and solid humic acid as adsorbents. Bicarbonate, tannic acid, and soluble humic acid were used as ligands. The model demonstrated strong influences of pH on the distribution coefficient for particulate vs. aqueous metal. Sibley and Morgan (1976) have carried out computations for a 16-metal, 8-ligand inorganic mixing model of oxic fresh and marine waters. SiO_2 was used as adsorbent in an AHIS model. In fresh water environments, the models showed competition between adsorption and aqueous complexation in determining trace metal speciation. The computations showed low adsorption of trace metals in seawater due to competition from Na^+, Mg^{2+}, and Ca^{2+}, and to chloride complexation of a number of metals. These results are somewhat at variance with the findings of Schindler(1975).

In this report we present results of computations for three natural water system models:

I. An AHIS model of an oxic 13-metal, 7-inorganic ligand system, with $SiO_2(s)$ as major adsorbing surface and with $MnO_2(s)$ and $Fe(OH)_3(s)$ as auxiliary adsorbents. Organic ligands (EDTA, citrate, histidine, aspartate, and cysteine) are included to demonstrate influences of strong complexation. Representative results for trace metal speciation as a function of surface area of SiO_2 adsorbent (pS is negative log of surface area expressed as hectare/liter) are given in the accompanying figure.

II. An AHIS model for the components of model I, but under anoxic conditions of the kind encountered in fresh water sediments.

III. An SCF model for aerobic dilute lake waters containing SiO_2 as model adsorbent and the ligands salicylate or citrate as model organic complexing agents. The metals included are: Ca, Mg, Fe(III), Mn(II), Cu(II), Cd, Zn, Ni, and Pb(II); inorganic ligands are carbonate, sulfate, chloride, ammonia, phosphate, silicate, and nitrate. Distributions of species are examined over the pH range from 4 to 8.



Speciation of trace metals in natural fresh waters in the presence of organic ligands (pCIT=pEDTA=pCYST=pHIS=pASP=6.0) as a function of surface area of $SiO_2(s)$ in ha/ℓ.

Detailed results of these three complex-system models will be discussed with respect to the following points: (1) distributions of trace metals as a function of pH; (2) effect of characteristics of different adsorbing surfaces; (3) adsorption in function of surface area; (4) effect of redox environment on the balance of adsorption-complexation-precipitation processes.

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ENVIRONMENTAL PHYSICS AND CHEMISTRY OF AQUATIC POLLUTANTS

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Classically, the removal or transformation of pollutants in the aquatic environment, -- the so-called "self-purifying" action of natural waters, -- has been ascribed to biochemical activities. Certainly, such activities are of major importance when the principal form of aquatic pollution is domestic wastes. However, as the production and use of synthetic chemicals has increased rapidly in the past few decades, pollution from these materials has become more and more important. Since a widespread characteristic of these anthropogenic substances is resistance to biological oxidation, the role of physical and chemical properties in the transformation and fate of aquatic pollutants is becoming more and more important.

I. PHYSICAL TRANSFORMATIONS

The physical properties that are particularly important in connection with the ultimate fate of polluting materials are volatility, solubility and adsorptive tendency. Since each of these properties is in some way a measure of pressure to escape from the aqueous medium, some correlation of them may be expected and some overlap of their operation in environmental transformations is to be expected.

(a) Volatilization. There seem to be no general quantitative studies on the transfer of volatile polluting materials from the aqueous to the gas phase. Rook and coworkers (1) have noted an overall drop in volatile organic material in the Rhine as indicated by headspace analysis from 1.6 mg per liter at Mannheim to 1 mg. per liter at Wiesbaden, 0.5 mg per liter at Koblenz, 0.3 mg per l. at Dusseldorf, 0.2 mg per l. at Ochten and <0.1 mg per l. at Schoonhoven just before the river reaches the industrial complex of Rotterdam. Because the changes were occurring in materials like benzene, toluene, dichloroethane and octanes, it has been suggested that the major pathway of loss of these compounds is by volatilization. A similar study (2) on water impounded for 20-30 days prior to use for Rotterdam water supply showed losses of 90% in headspace volatiles during the summer period and of approximately 70% in the winter season.

It is difficult with studies like these to be certain that the processes operating are those postulated. Some evidence that the losses are not the result of biological oxidation is provided by the independent studies of Kolle (3) and of Kolle, Koppe and Sontheimer (4). These workers showed, by means of C^{14} measurements, that the organic content of the Rhine shifted gradually from currently photosynthesized materials in the upper reaches to nearly 80% petroleum-derived compounds at Dusseldorf. The dominance of petroleum-based materials served not only to indicate the industrial pollution of the Rhine, but also their persistance against biological oxidation.

The conditions of Rook's studies were such that loss of these small molecules by adsorption was not likely. Some form of photooxidation cannot be ruled out as the mechanism for losses of the materials from aqueous solution, but seems less plausible than volatilization in view of the pattern of the losses.

That the rates of loss of these materials by volatilization is not unreasonable is indicated by the laboratory studies of Mackay and Wolkoff (5) Dilling, Tefertiller and Kallos (6) and Mackay and Leinonen (7). The last of these sets of workers showed, in particular, that many organic pollutants of low molecular weight exhibited transport properties giving half-lives for volatilisation of 5 to 10 hours for a one-meter depth of water. Dilling and coworkers showed short half-lives also for numerous chlorinated hydrocarbons.

Not all organic compounds of low molecular weight vaporize so readily, however. A classic instance is the tracing of o-nitrochlorobenzene for 1000 miles down the Mississippi River from St. Louis to New Orleans by personnel of the U.S. Public Health Service (8). It may be that volatilization was inhibited in this instance by adsorption of the nitrochlorobenzene onto suspended clay or other mineral particles being transported by the river. In this regard it seems likely that adsorption will often act antagonistically to evaporation.

(b) Precipitation. Particularly when trace pollutants are under consideration, it is difficult to separate direct precipitation from adsorption as transforming mechanisms. Both involve a transfer of material from the aqueous phase to the solid phase, and both will show reductions in aqueous concentration when samples are filtered or allowed to settle. Firm differentiation seems possible only when it can be shown that the aqueous solubility of the pollutant in question is greater than its concentration in the water being examined. Quantitative aqueous solubility data are not generally available, however, for trace pollutants of low solubility.

One series of compounds for which precipitation phenomena may be of importance is the polynuclear aromatic hydrocarbons. These have been found to be principally present in a number of waters in suspended rather than dissolved condition. For example Lewis (9) in his study of 5 polynuclear aromatic hydrocarbons in several British rivers observed that in those samples with total polynuclear aromatic hydrocarbons greater than about 10 mg per l., 50 to 90% of the material was present in the suspended fraction. It could be removed by laboratory filtration or by the standard coagulation-filtration process of water treatment.

Whether the suspended material is clay with adsorbed PAH or precipitated PAH is not certain. Some observations by the Netherlands Government Institute for Water Supply (10) have indicated that the concentration of PAH in rainwater in the vicinity of Rotterdam is several times the concentration in the Rhine, suggesting that the PAH is in suspended particulate form before it reaches the silt-bearing water courses. They may still be adsorbed on soot particles, however. Also, the observation by Borneff (11) that ozonation or chlorination is only partially effective in removing PAH is in accord with the particulate occurrence of much of it in water. Penetration of particulate matter is poor with low concentrations of ozone, especially.

(c) Adsorption. The adsorption of trace pollutants on clay minerals and other particulate matter is probably a major factor in the transport of certain aqueous pollutants into sediments, but is one of the most difficult factors to provide quantitative data for. The variety of potential particulate adsorbents is great, the concentration in any natural body of water may vary greatly and at times quite suddenly, depending on the weather and the adsorptive property for any one pollutant is interactive with those of all other pollutants present. Qualitatively, however, it is clear that much of the transfer of aqueous metallic pollutants and of non-volatile organic substances to the sediments that occurs when rivers are impounded or become quiescent is the result of adsorption.

II. CHEMICAL TRANSFORMATION

Types of chemical reactions that are of general interest in connection with the breakdown of organic pollutants in aqueous solution include hydrolysis, direct oxidation by O_2, catalyzed oxidations, photolysis, photooxidation and photosensitized oxidations. Other types of reaction are possible, particularly in anoxic waters, but have not been investigated with trace pollutants in sufficient detail to make consideration useful.

All of the types of reactions are likely to be affected in their rates by both temperature and pH, the latter either by its effects on acid-base equilibria of the pollutant or by participation of H^+ or OH^- in the reaction as catalyst or reactant. So, these environmental factors are important parameters in assessing the significance of chemical transformations.

(a) Direct oxidation. Apart from the transformations of simple inorganic materials like Fe^{++}, Mn^{II} and H_2S, direct oxidation by O_2 appears to play a very small role in the oxidation of aquatic pollutants. If an organic pollutant is susceptible to significantly rapid direct oxidation by O_2 it is almost certain to be even more susceptible to biologically mediated oxidation. The latter will generally be dominant in environmental aquatic systems unless some factor is present to maintain sterility in the system.

Rates of direct oxidation are of chief interest to set minimum rates of transformation in material waters for modelling or prediction. In general rates are greater, or duration times less, as a result of biochemical activity.

(b) Catalyzed oxidations. Although direct oxidation of organic pollutants by O_2 is normally slow, the oxidation may be brought about by other oxidants that are subsequently reoxidized by O_2 itself. Thus, Morgan and Stumm (12) and Theis and Singer (13) have discussed the iron-catalyzed oxidation of aqueous phenols by O_2, in which ferric iron is the actual organic oxidant, with the product ferrous iron being reoxidized by O_2. It appears that manganese may act similarly.

(c) Photolysis. It has been known for a long time that light may have a strong effect on the transformation of organic substances in water, even though the mechanisms remain obscure. Humic and fulvic acids, the source of the natural stain in water, are strongly resistant to biological degradation as is shown by the persistence of color in natural waters. It has also been noted, for example, that somewhat more than half the total organic carbon remaining in sewage effluents after efficient secondary biological treatment of municipal sewage is humic and fulvic acids (14).

During the first two decades of this century extensive investigation of the behavior of organic color in reservoirs showed that there was a light-induced bleaching of the color that amounted to about 50% per month for the surface layers during New England summers (15). The nature of this photo reaction has not been studied, however, and so the fundamental changes that produce the loss in color are not known.

There are three general types of light-initiated processes that seem to have significance for the transformation of aquatic pollutants:
(a) photolysis, in which light absorbed by the pollutant leads to its decomposition into more reactive fragments. These fragments are considered often to be free radicals that may stimulate considerable oxidation through radical chains; (b) photochemical oxidation, in which excitation of the pollutant by light is followed by formation of singlet oxygen, which then serves as a more active oxidizer than normal O_2; (c) photosensitized oxidations, in which the initial step occurs as in (b), but then the singlet O_2 initiates the oxidation of a compound other than the one that was excited initially. All three of these processes may be active in the

light-induced oxidation or transformation of pollutants. Until now, however, studies have not been sufficiently detailed to delineate mechanisms precisely.

Among the compound known to undergo light-induced reactions in dilute aqueous solution are benzo [α] pyrene (16), metallic complexes of nitrilotriacetate and ethylenediaminetetraacetate (17)-(20), 2,4-D esters (21) and pesticides (22) (23). Moreover, Paris, Lewis and Wolfe (24) have described the photosensitized oxidation of malathion in which natural humic acid is the photosensitizer. The half-life for photodecomposition was reduced from 990 hours to 15 hours in the presence of humic acids.

(d) Hydrolysis. Hydrolysis is most significant as a mode of environmental transformation of anthropogenic pollutants for organic esters--phthalate esters, herbicide esters, phosphates and others. Hydrolysis of these materials is generally acid-base catalyzed so that the times required for hydrolysis are very much dependent on pH. Hydrolysis often leads to complete oxidation or degradation, for the organic acids or alcohols that constitute the hydrolysis products tend to be more readily broken down biologically than the parent esters are.

There are excellent studies on the hydrolysis of 2,4-D esters and Malathion (21) (25). The study on the 2,4-D esters, in particular, is a model of the sort of broad investigation of physical and chemical properties that needs to be conducted for any pollutant if its ultimate environmental fate is to be defined or predicted. The investigation covered not only the hydrolysis reaction as a function of temperature and pH, but also the vaporization process and photooxidation. Other, less significant properties were also considered, though they were not studied as thoroughly. Of the potentially important transformations, only the role of adsorption and transport to the sediments was not covered. All in all, it appears possible now to present a nearly complete picture of the environmental fate of 2,4-D esters. Similarly detailed data for other compounds would be most welcome.

III. SUMMARY

For many conservative or anthropogenic pollutants physical or chemical properties determine environmental transformations and fate. There is a great need for fundamental physical and chemical data that can be related to the behavior of aquatic pollutants under environmental conditions.

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ENVIRONMENTAL TRANSPORT MODELING OF POLLUTANTS IN WATER AND SOIL[1]

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In considering the processes and critical data for evaluation of pollutant transport, one must consider the source of the pollution, how it is injected into the ecosystem, whether the injection of that pollutant is via aerial or terrestrial pathways, whether the origin is of point source nature or area source nature, and whether it is directed toward the surface of the landscape or injected directly into the hydrologic system. The chemical form of the constituent is also of great importance. We will be considering today mainly the transport of solids which can be solubilized or can be transported as particulates. Soluble forms of the heavy metals will be considered to undergo first-order exchange, and other non-exchangeable types of any metal will be transported in particulate form as sediment.

The time scale to be considered in modeling pollutants can vary dramatically from a few seconds to several years. However, for most of those materials of current interest, we think in terms of attempting to simulate time periods on the order of a year. Weathering processes, of course, are natural geologic processes on the time scale of thousands of years. At the other end of the spectrum, kinetic transformations of many very highly reactive substances are such that 99% of the reaction may be complete in the order of a minute. Generally, however, the very short time period transformation reactions are not of interest for pollutant transport because the initial product that is being considered quickly disappears from the system. More persistent chemical forms which last on the order of a year can pose a threat to the health of man or to the environmental health of the ecosystem.

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Models which address these transport calculations are as varied as is the time scale. Many of these models address an extremely small part of the total ecosystem and are directed at transport in a limited physical space. Such models can be characterized as mathematically interesting and, in certain cases, useful for analysis of the system. However, we have tended overall to study larger geographic areas in order to show interrelationships among a variety of physiographic and environmental processes. We have employed transport models which are oriented toward a watershed basis, in which the area considered varies from one acre through several thousand square miles. These watersheds require the application of models which consider the complete range of environmental processes, starting with infiltration of water through soil, proceeding through evapotranspiration to runoff from the soil surface or runoff in the form of base flow to the stream channel, as illustrated in Fig. 1. Each one of these hydrologic processes is capable of carrying pollutant material in dissolved or particulate form. In fact, within the soil surface the process of evapotranspiration leads to the drying of a toxicant causing it to move from a lower level to a higher level. Further wetting would reverse the flow toward the deeper regions.

Through experience we have found that we need models of the entire hydrologic cycle in order to model the influence of the daily and seasonal variation in precipitation. The model which provided a basis for many of our first studies of toxicant transport was the Stanford Watershed Model of N. H. Crawford and R. K. Linsley [1966], as adapted by D. D. Huff [1968], presently at the Oak Ridge National Laboratory in the Environmental Sciences Division. We called this model the Wisconsin Hydrologic Transport Model [Patterson et al, 1974] and used it to study the transport of a variety of heavy metal ions in the vicinity of fossil fueled power plants. We also studied metal ions emitted as particulates near a lead smelting plant [Patterson et al, 1975]. We have adapted the model further to consider the transport of particulates that are entrained in water by soil erosion processes and by direct deposition into the water. The study of these particulates, for example depleted lead ore, is important because their movement constitutes in some cases the largest mass flow for material we have studied. Particulate transport then provides the main source of material to downstream processes.

Models of the type that we have described require considerable amounts of information in order to be effective; however, even more detailed studies in the near vicinity of structures such as a smeltering plant can be effected by using a detailed formulation of the soil moisture equation and its associated transport of soluble material within soil. This type of model has also been studied at ORNL by M. Reeves and J. O. Duguid [1975] who have evolved a finite element code, which is sophisticated in terms of solving the soil moisture equation and is based on the method described by Pinder and Frind [1972]. It is presently limited to the consideration of relatively localized areas of contaminated soil because it requires the conductivity, permeability, and exchange to be the same in each vertical layer of soil. Extensions of this method have been made by Gupta, Tanji, and Luthin [1975]. The finite element is unexcelled in terms of considering the effect of soil type, texture, and permeability on water movement.

We have found that to first order the effect of heavy metal ion mobility in soil can be modeled by a simple exchange coefficient k_d [Begovich and Jackson, 1975]. This exchange coefficient plus considerations for bulk transport and for the initial solubility of the toxicant allow one to establish a budget for the toxicant. The other processes that must be considered in addition to those already mentioned include the sedimentation which occurs when the toxicant reaches the stream channel.

To summarize, the processes that we have found to be important in pollutant transport in terms of transport modeling include the surface flow of a material either as a solute or in bulk form, and the solubilization of the toxicant by incident precipitation, initial infiltration into the soil, the evapotranspiration processes, the subsequent exchange of the cations from the solubilized toxicant, and leaching through soil of the cations which are undergoing transport. The critical data can be inferred from these processes to be the particle size distribution for the toxicants, the solubilities of toxicants, the permeability of the soil horizons involved, and the values of the exchange coefficient k_d. The hydrologic properties that are also critical in determining the entrainment and subsequent transport of the toxicants on a watershed scale can be summarized as streamflow data, that is data that relates to the streamflow volume, its velocity, the width of the stream, depth, the length of the reaches that make up various segments of the river channel system.

We have used the UTM to study heavy metal transport in the vicinity of a lead smelter in southeast Missouri. In this particular application, four heavy metals including lead, cadmium, zinc, and copper were considered. They are input by atmospheric deposition to the landscape surface. The model used in this simulation was the SCEHM model (Soil Chemistry Exchange of Heavy Metals) which was coupled into the Wisconsin Hydrologic Transport Model to provide input deposition values and to obtain values for precipitation, surface flow, soil moisture content, and soil moisture flux. Figure 2 illustrates various moisture and contaminant fluxes and contaminant exchange within each of the homogeneous soil chemistry layers. Figure 3 shows six years of simulated values for lead in the A1 horizon, which is that part of the soil from 0-3 cm, and in the A2 horizon (3-15 cm) on Crooked Creek Watershed. The exchangeable lead is building up in the soil because of the high soil exchange coefficient (k_d) for lead. Lead continues to accumulate on this watershed because the solubility of the lead is not sufficient for it to be removed from the watershed in surface flow or as the water percolates through the soil profile. In addition, by comparing simulated and experimental results, we have concluded that insoluble lead is infiltrating into the soil in particulate form. In contrast to the build up of lead, we see in Fig. 4 that cadmium in the A1 and A2 horizons is depleted during rainfall events and rainy seasons and that it has gradually built up to asymptotic values in the A1 horizon and has almost reached an asymptotic level in the A2 horizon. Similarly for zinc, in Fig. 5 we see that it also has sufficient solubility and a low enough exchange coefficient to percolate through the soil and lead to the establishment of the steady state concentration value in the surface 3 cm of the soil. Finally in Fig. 6, we see the values for the copper plotted for the six year period of the A1 and A2 horizons and note that copper's behavior is very like that of lead in that it is built up and continues to build up during the six year period. It exhibits slightly more response than lead to rainfall during months of heavy rain.

We believe that this model is most valuable in predicting buildup of heavy metals which remain as free ionic cations after dissolution and during infiltration through the soil. This study points out the different mobilities that can occur from different materials, which may force a different emphasis on the transport model in order to consider that given substance. For example, an extremely mobile compound may require a major emphasis be given to transport in the aquatic system in the stream channel if the compound is not complexed by the soil and if it is readily solubilized. Other conditions could force consideration of the effect of vapor pressure, since vapor pressure of the material can interact very strongly with environmental conditions such as wind speed and turbulence to affect the rate at which the material is dispersed into the environment from terrestrial and aquatic phases. Thus the interaction of the landscape with the aquatic system can lead to formation of a new species, to complexation with the soil, or to passive transport through the pores of the soil and in the aquatic system.

We feel that it is very useful in our studies to have available an integrated transport model such as the Wisconsin Hydrologic Transport Model which allows us to consider a variety of processes that are important in watershed scale transport. We feel that the simplicity of the processes modeled here have aided us in gaining insight into the pathways taken by these toxicants as they flow through the ecosystem. In addition, we have found that we can couple models of plant growth to these transport models and attempt to assess the effect on growth rates due to the entrained toxicant and uptake of that toxicant by the plant. The availability of the general model is useful also because the characteristics of pollutants are variable, and one can study the response of the terrestrial or aquatic system to input of toxicants of varying natures.

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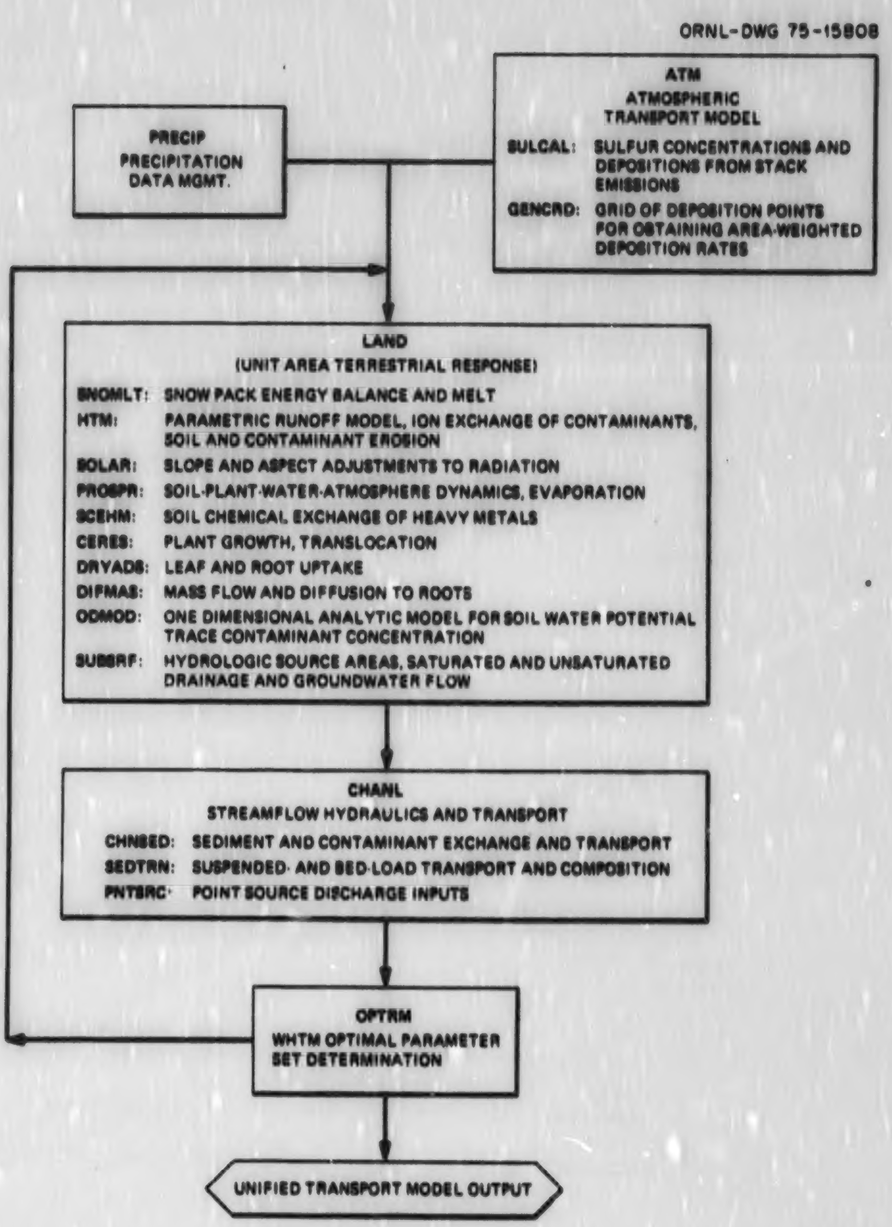
ORNL-DWG 75-15808
PRECIP
PRECIPITATION DATA MGMT.
ATM
ATMOSPHERIC TRANSPORT MODEL
SULCAL: SULFUR CONCENTRATIONS AND DEPOSITIONS FROM STACK EMISSIONS
GENCRD: GRID OF DEPOSITION POINTS FOR OBTAINING AREA-WEIGHTED DEPOSITION RATES
LAND
(UNIT AREA TERRESTRIAL RESPONSE)
SNOMLT: SNOW PACK ENERGY BALANCE AND MELT
HTM: PARAMETRIC RUNOFF MODEL, ION EXCHANGE OF CONTAMINANTS, SOIL AND CONTAMINANT EROSION
SOLAR: SLOPE AND ASPECT ADJUSTMENTS TO RADIATION
PROSPR: SOIL-PLANT-WATER-ATMOSPHERE DYNAMICS, EVAPORATION
SCEHM: SOIL CHEMICAL EXCHANGE OF HEAVY METALS
CERES: PLANT GROWTH, TRANSLOCATION
DRYADS: LEAF AND ROOT UPTAKE
DIFMAS: MASS FLOW AND DIFFUSION TO ROOTS
ODMOD: ONE DIMENSIONAL ANALYTIC MODEL FOR SOIL WATER POTENTIAL TRACE CONTAMINANT CONCENTRATION
SUBSRF: HYDROLOGIC SOURCE AREAS, SATURATED AND UNSATURATED DRAINAGE AND GROUNDWATER FLOW
CHANL
STREAMFLOW HYDRAULICS AND TRANSPORT
CHNSED: SEDIMENT AND CONTAMINANT EXCHANGE AND TRANSPORT
SEDTRN: SUSPENDED- AND BED-LOAD TRANSPORT AND COMPOSITION
PNTSRC: POINT SOURCE DISCHARGE INPUTS
OPTRM
WHTM OPTIMAL PARAMETER SET DETERMINATION
UNIFIED TRANSPORT MODEL OUTPUT

Fig. 1. The Submodels That May Be Linked to Form A Unified Transport Model.

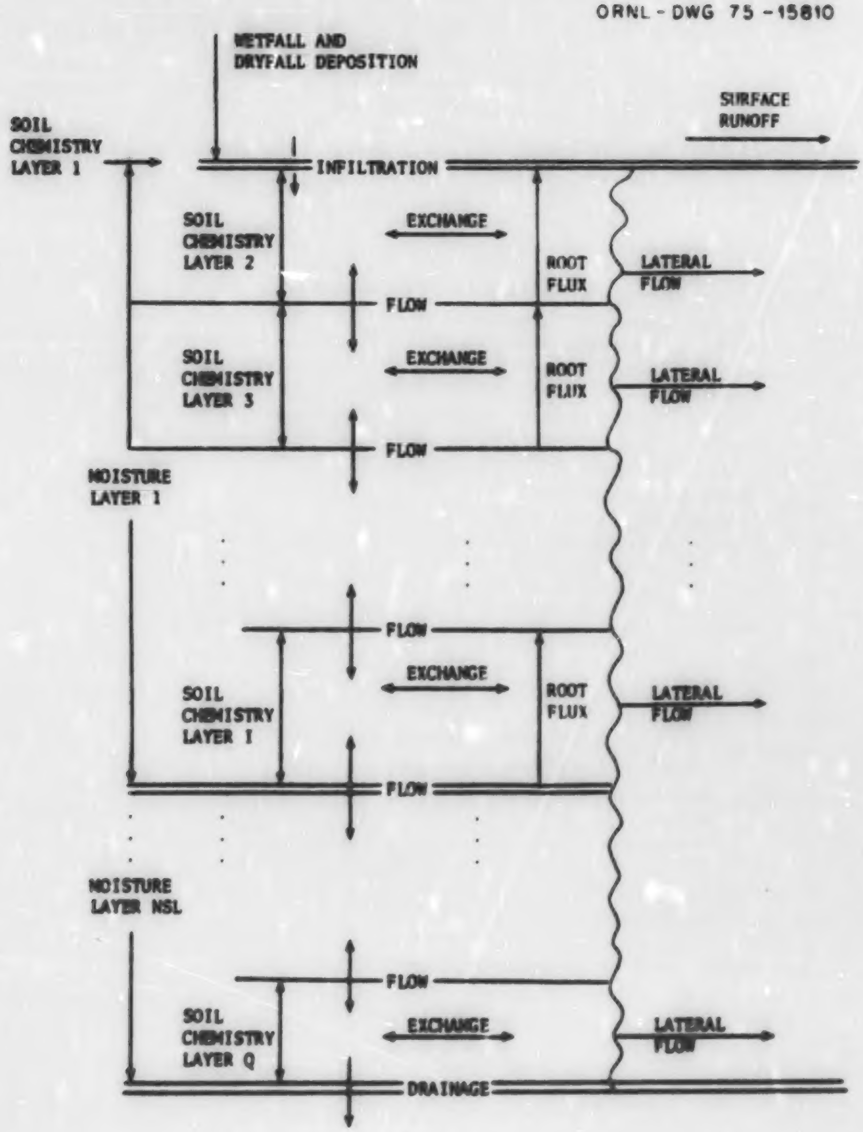
ORNL-DWG 75-15810
WETFALL AND DRYFALL DEPOSITION
SOIL CHEMISTRY LAYER 1
SURFACE RUNOFF
INFILTRATION
SOIL CHEMISTRY LAYER 2
EXCHANGE
ROOT FLUX
LATERAL FLOW
FLOW
SOIL CHEMISTRY LAYER 3
EXCHANGE
ROOT FLUX
LATERAL FLOW
FLOW
MOISTURE LAYER 1
FLOW
SOIL CHEMISTRY LAYER I
EXCHANGE
ROOT FLUX
LATERAL FLOW
FLOW
MOISTURE LAYER NSL
FLOW
SOIL CHEMISTRY LAYER Q
EXCHANGE
LATERAL FLOW
DRAINAGE

Fig. 2. Schematic of SCLHM.

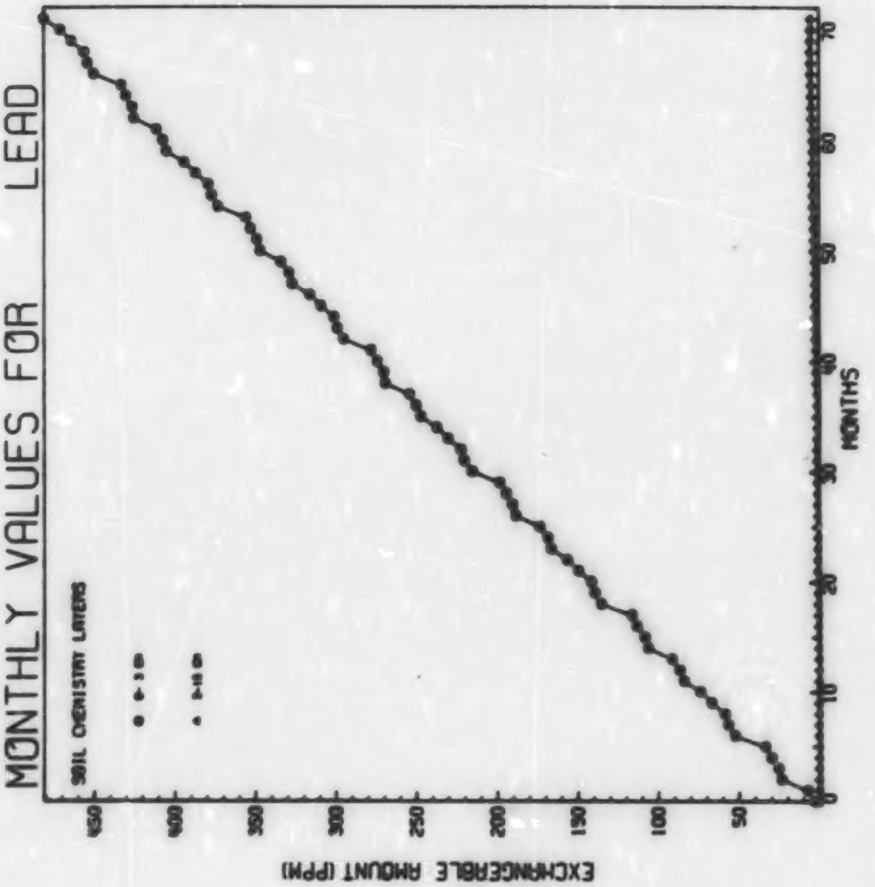

Fig. 3. The Amount of Exchangeable Lead in the *A1* (0-3 cm) and *A2* (3-15 cm) Horizons for the Six-Year Simulation Run on Crooked Creek Watershed.

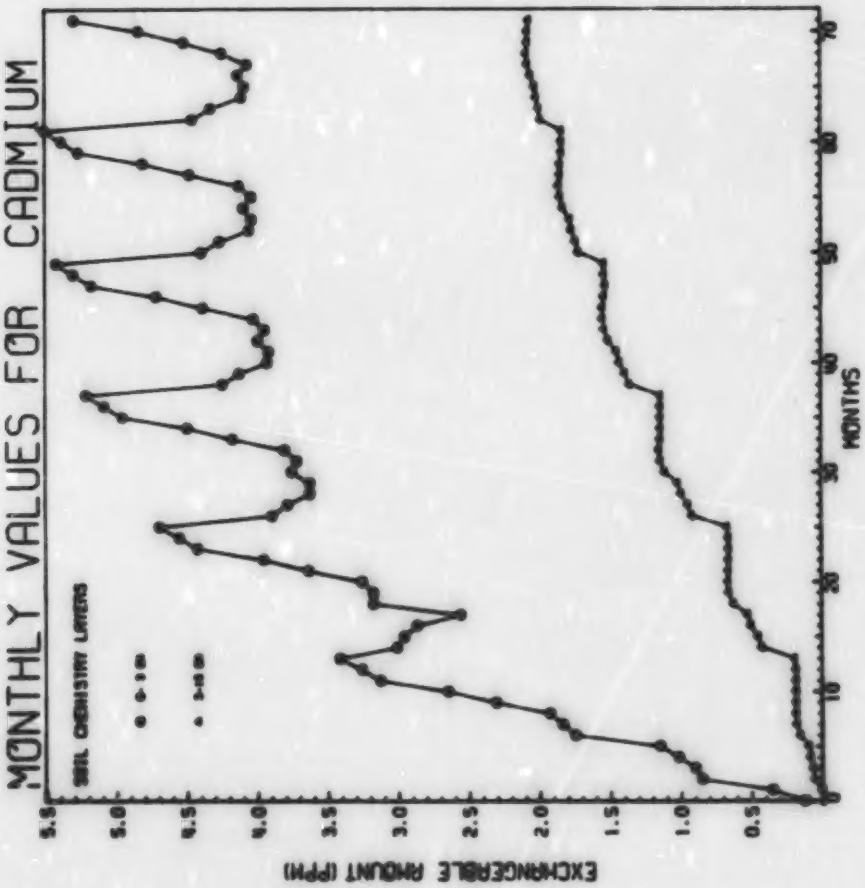

Fig. 4. The Amount of Exchangeable Cadmium in the *A1* (0-3 cm) and *A2* (3-15 cm) Horizons for the Six-Year Simulation Run on Crooked Creek Watershed.

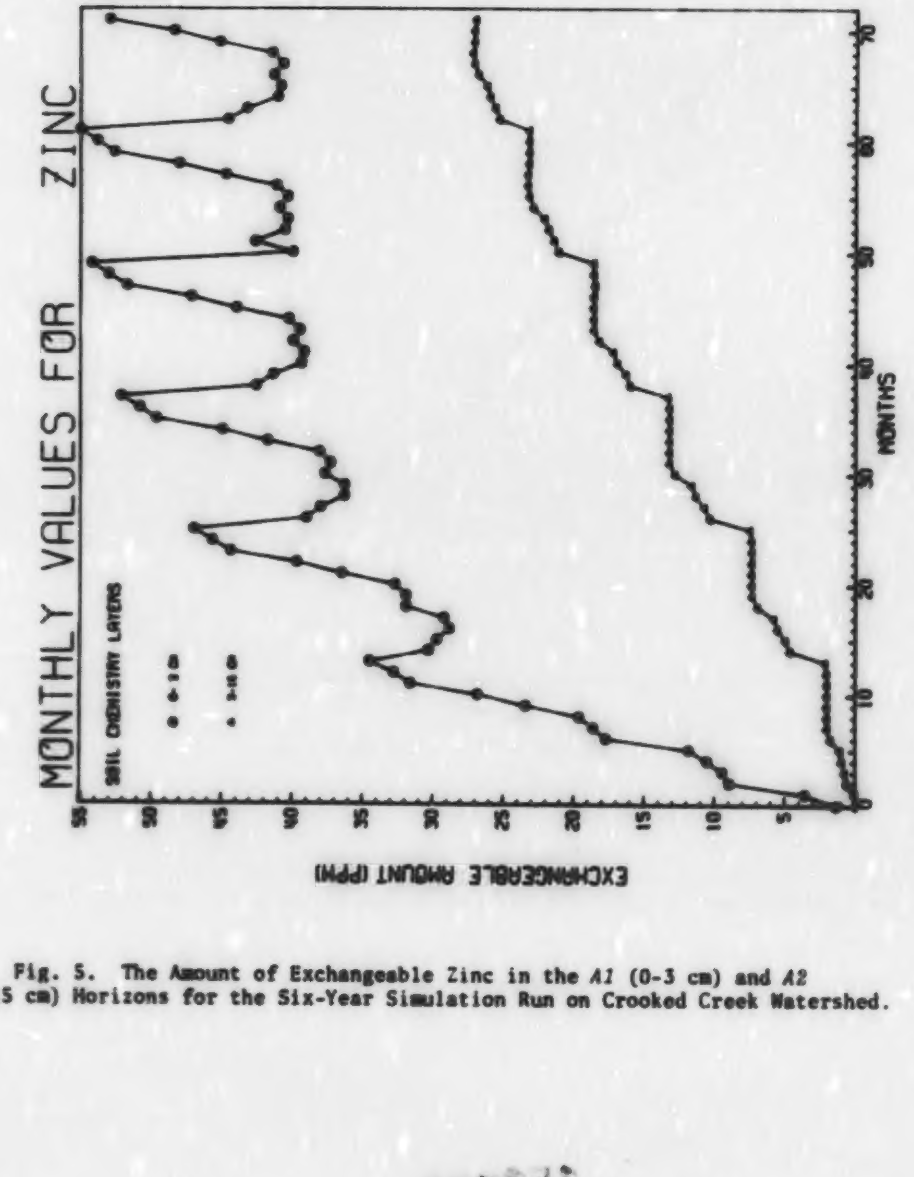

Fig. 5. The Amount of Exchangeable Zinc in the *A1* (0-3 cm) and *A2* (3-15 cm) Horizons for the Six-Year Simulation Run on Crooked Creek Watershed.

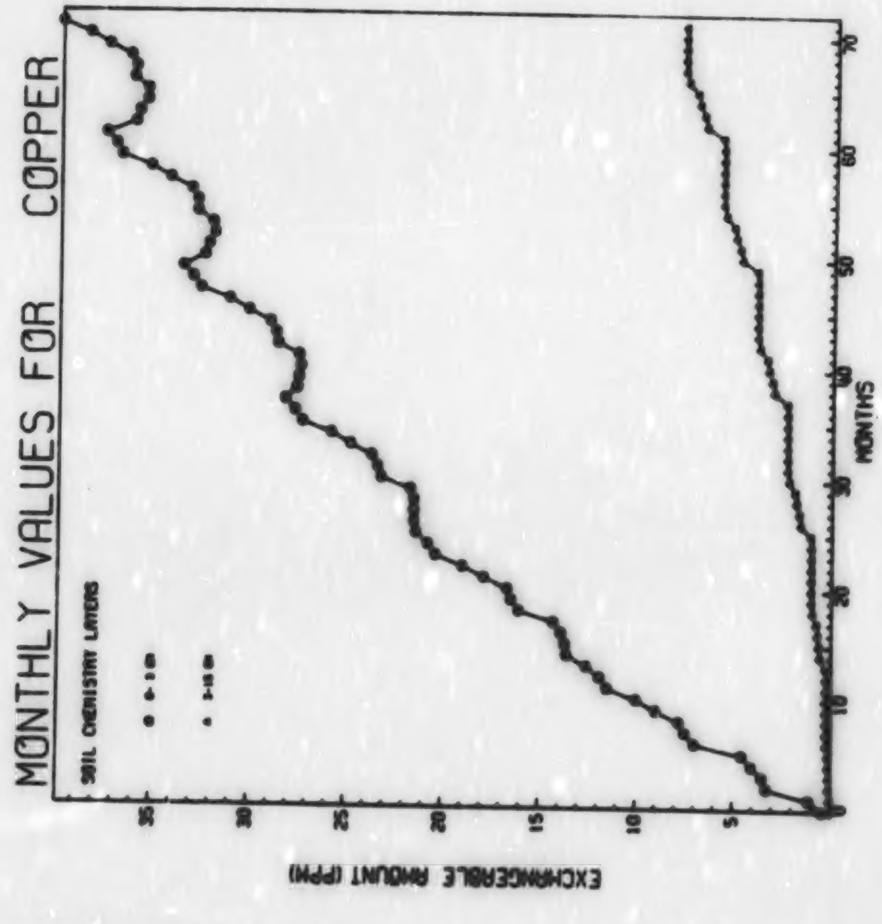

Fig. 6. The Amount of Exchangeable Copper in the *A1* (0-3 cm) and *A2* (3-15 cm) Horizons for the Six-Year Simulation Run on Crooked Creek Watershed.

OXIDATION AND REDUCTION OF PESTICIDES IN SOILS AND SEDIMENTS

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Many pollutants are characterized by their resistance to oxidation, reduction or other chemical reactions. The stability of most pesticides during storage indicates that normally they are quite resistant to chemical decomposition. Nor are suitable conditions for chemical degradation often encountered in the environment and we must regard decomposition by microbial action or by sunlight as primary routes by which degradation of field-applied pesticides occurs. In the absence of quantitative information, however, it is useful to analyze some environmental processes to see whether biological and nonbiological transformations can be distinguished and to what extent they are interdependent.

Soils and sediments are complex media. They contain complex minerals and metal salts intimately associated with organic matter. The heterogeneity and polyfunctional nature of soil macromolecules has made the problem of structure elucidation an arduous task for the organic chemist. The application of modern instrumental techniques and a renewed interest in geochemistry have spurred progress in recent years.

The organic matter content of sediments is about 0.7%. This is largely in the form of insoluble polymeric material known as 'kerogen'. Kerogen is an extremely insoluble, heterogeneous material and it is presumably highly cross-linked. Organic matter in this state is also strongly associated with neighboring molecules through dipolar interaction and hydrogen bonding. It presents a very unattractive proposition for study by the organic chemist. Such organic compounds will be intimately associated with the inorganic fraction and in some cases they may be enclosed in expanded clay lattices.

The aquatic system provides a means for degradation by sunlight irradiation, oxidation, etc. and the organic matter in the sediment may not be typical of that in the biomass above. Eglinton has summarized the situation: "Most organically-rich recent sediments are reducing but there is generally an oxidizing zone in the upper layers of the sediment and the water column above it". Biological activity that results from the introduction of microorganisms and other forms of life makes it difficult to distinguish between organic compounds extracted from the living organisms and those extracted from the non-living components of the sediment. As the depth increases and the sediment is compressed, biological activity falls to zero. Organic matter distribution in recent muds approaches that in ancient shales. Most of the organic matter is an insoluble, polymeric condensed material. Hydrocarbons are present and their composition is indicative of their biological origin. During a relatively short time period molecules may be transformed by biological or nonbiological processes. One major distinction between the two processes is that the former generally involve controlled synthesis or degradation, whereas the latter lack the orientational selectivity and stereochemical specificity that generally characterize enzyme reactions.

Oxidation and reduction reactions in soils and sediments are primarily biological. Microorganisms in soils and sediments are the agents mainly responsible for transformation of pesticides. Soil moisture content, pH, temperature, aeration, and ion exchange capacity influence the nature of the soil microbial population and thus the nature of the metabolic products. In the well aerated upper layers of soil the microbial population consists of aerobic organisms that derive their energy from oxidative reactions. Below a water surface in a sediment rich in organic matter, the microbial population alters as oxygen is depleted. The population of facultative anaerobic microorganisms increases and finally, obligate anaerobic species predominate. These events can be followed in a sedimentary system by measuring the fall in redox potential.

Attempts to make the distinction between chemical and biological reactions in soil media by performing experiments in sterile soils have usually met with much criticism. Autoclaving is normally adequate for sterilizing glassware or equipment contaminated with microorganisms. However, sterilization of soil may affect not only the microbial population but also the chemical and physical structure of the medium. Thus, nonbiological processes may be precluded as a result of such treatment. The use of microbial inhibitors, fumigants, irradiation, or other methods of reducing microbial activity are equally open to criticism. These techniques often result in substantial changes in soil reactivity or the presence of reactive residues.

Although direct evidence for chemical, as opposed to biological, degradation of a pesticide may be lacking, sometimes we may infer that chemical degradation occurs if we cannot identify soil microorganisms specifically capable of degrading the molecule in question. Degradation of 3-amino-1,2,4-triazole (amitrole) in sterile and nonsterile soils gave carbon dioxide as a product. Degradation in sterile soils occurred when the soil had been sterilized by azide or ethylene oxide, but not when the soil had been autoclaved. Addition of the sodium salt of ethylenediaminetetraacetic acid to nonsterile or ethylene oxide treated soils reduced the rate of degradation. Many unsuccessful attempts have been made to isolate or identify microorganisms capable of degrading amitrole, suggesting either that special conditions are necessary for microbial degradation or that reaction is purely chemical.

The chemistry of the degradation process has been elucidated. Amitrole is resistant to many powerful chemical oxidants, but, in the presence of free-radical generating systems, the ring was ruptured yielding carbon dioxide, cyanamide and urea. These products were also formed when a solution of amitrole in water was irradiated with ultraviolet light of wavelength ca 220 nm. There was no reaction at long wavelengths (> 310 nm) until riboflavin was added to the solution. Reaction with Fenton's reagent gave the same products, indicating that amitrole readily undergoes oxidation by free radicals. Although interesting parallels may be drawn from these observations, the above evidence is no more than circumstantial.

Free radicals are present in soil. Some of these are associated with the humic acid fractions. It has been proposed that their formation and properties are intimately associated with the nature of the silicate environment, since the EPR signal widths vary widely in humic impurities found in different clay types. Other soil components such as lignins, tannins, resins, pigments and antibiotics contain free-radical species. Steelink et al proposed that a model for the radical species in the humic fraction of soil based on an ortho-and para- quinhydrone-containing polymer would account for many of the observed properties.

The role of free radicals in soils remains to be established. They may inhibit one-electron metabolic processes, scavenge halogen-containing compounds or catalyze polymerization reactions.

Although it may be very difficult to distinguish between biological and chemical changes in soils and sediments in most natural situations, a combination of both types is expected. Generally the former take place in aqueous media at ambient temperature and are catalyzed by complex macromolecules, whereas the latter give similar products only under conditions of temperature, acidity or alkalinity unfavorable to life. However, the action of biota on xenobiotic molecules often gives terminal products that result from a combination of biological transformations and thermal reactions. The products of biological reaction are frequently quite reactive and may undergo subsequent chemical reactions spontaneously, following an initial metabolic step. Although these are not strictly 'non-biological' reactions, much of the driving energy for environmental chemical reactions is derived from solar energy or from the proximity of biological systems and such reactions will be significant.

Transformation of organic molecules in plants, vertebrates or higher organisms often involves a complex series of reactions in which the molecule undergoes minor modifications and is ultimately 'conjugated' to yield a compound of high molecular weight. Elimination or 'detoxication' often involves conjugation with water-soluble polar residues of biological origin, such as sugars, amino acids, oligosaccharides, peptides, etc. New functional groups (hydroxylation of aromatic systems, etc.) which favor subsequent conjugation reactions may be formed through the intermediacy of enzymes such as the mixed function oxidases. These routes may also be accompanied by pathways involving more substantial disruption of the molecule. Degradation products containing one or two carbon atoms may be utilized as starting points for the elaboration of biological macromolecules or may be eliminated as carbon dioxide.

By contrast, transformations of complex organic molecules by soil bacteria normally result in degradation to carbon dioxide, water, nitrogen, chloride ions and other inorganic ions as ultimate products. This is referred to as 'mineralization' and there is an optimistic belief that such a self-cleansing process will continue to rid the environment of undesirable compounds. However, complex intermediates formed in some bacterial processes may subsequently undergo purely chemical reaction to give unanticipated products.

The metabolism of chloroanilines derived from aniline-based herbicides provides an example. In soil, these slowly evolve carbon dioxide, indicating disintegration of the aromatic ring. However, azobenzenes are detected as soil residues and these can only result from the condensation of two molecules of aniline. *Fusarium oxysporum* Schlecht, a fungus present in soil, is capable of effecting the oxidation of a primary aromatic amino group to a phenylhydroxylamine. If 4-chloroaniline is used as a substrate, the rapid formation of 4-chlorophenylhydroxylamine can be demonstrated by color reactions. 4,4'-Dichloroazoxybenzene can be isolated from the medium. (Attempts to isolate 4-chlorophenylhydroxylamine during chemical synthesis by reduction of 4-chloronitrobenzene often result in the isolation of 4,4'-dichloroazoxybenzene, because this product is readily formed by the condensation of two molecules of the reactive hydroxylamine.) 4,4'-Dichloroazobenzene is a further product of metabolism. It is conceivable that condensation of an aniline and a nitrosobenzene represent a chemical route to this compound.

The formation of phenylhydroxylamine represents a major metabolic pathway, but other metabolic routes observed are: hydroxylation of the ring at the *ortho* position, acetylation or formylation of the aromatic hydroxy and amino groups. Hydroxylation at the *ortho* position of an aromatic amine is a well-known rearrangement reaction of phenylhydroxylamines. Thus, although we assume that this reaction is mediated by an enzyme system and that direct hydroxylation of the aniline ring occurs, we cannot exclude the possibility that the *o*-aminophenol is derived through a rearrangement of a phenylhydroxylamine.

Another interesting example is the formation of a triazene from propanil. Propanil (3,4-dichloropropionanilide) is rapidly hydrolyzed to the parent aniline, 3,4-dichloroaniline, in soils. One of its metabolites in soil under special cultural conditions is 3,3',4,4'-tetrachlorotriazene. This compound has *three* nitrogen atoms. The question of the origin of the third nitrogen atom is important because the only likely source is inorganic nitrite. This must be derived from the soil where its availability depends on bacterial nitrification processes. Synthetically, the triazene is prepared by diazotization of 3,4-dichloroaniline with nitrous acid followed by reaction with 3,4-dichloroaniline in the presence of sodium acetate as a buffer. In soil, the formation of the triazene strongly suggests the intermediacy of a diazo compound that must result from a reaction of aniline with inorganic nitrite. Thus we have a further example of a transformation which may be biological or chemical. If these reactions take place under conditions normally found in soil, *N*-nitrosation might be a frequent occurrence when appropriate secondary or tertiary amines are present.

Distinctions between 'biological' and 'nonbiological' reactions become extremely subtle as we continue to examine the types of reaction occuring in nature. Two important types of reaction are oxidation and reduction. If we consider an aquatic system containing sedimentary organic material, the upper layer will favor oxidative processes whereas the lower will favor reductive reactions.

The availability of oxygen and nutrients favor growth of biota. Their source of energy is based primarily on the oxidation of organic compounds using oxygen as an electron acceptor. Enzymic systems of microflora are generally capable of accomplishing a variety of oxidative reactions.

Excess oxygen and oxidants will also bring about reactions in the upper layers of an aquatic system. Activated processes of oxygenation such as photosensitized oxidation, oxidation by singlet oxygen, oxidation by transition metals, and radical oxidation processes are conceivable under these circumstances. The absence of oxygen at lower depths will favor microorganisms capable of utilizing other sources of energy and their survival will depend on anaerobic processes, i.e. metabolic reaction sequences will be based on electron acceptors other than molecular oxygen. Thus, reductive processes will predominate. The characteristic property of each depth region is its redox potential. Organic molecules will react as electron acceptors or donors depending on the redox potential of the medium without respect to its origin.

Rates at which reactions occur will depend on the homogeneity of the system, i.e. solubility of the substrate, adsorption of the substrate to interfaces where it is less reactive, and adsorption to interfaces where it is more reactive.

Oxidation

Oxidation is probably responsible for degradation of a substantial fraction of the pollutants present in aquatic systems and soils. Oxidation may occur by microbial action, photooxidation, direct attack of oxygen, or an activated oxidizing species. These factors will be affected by pH, soil type, metal ions, photosensitizers, oxygen content of the sediment, temperature, sunlight, etc. Microbial systems are responsible for many oxidative transformations. A number of complex catalytic systems involving metals can provide models for oxidizing systems. The products are similar to those from biological oxidation and there are close analogies between them in that they both involve the generation of activated species of oxygen.

Photochemical oxidation may also proceed through activated oxygen species. Autoxidation processes involve peroxy and alkoxy radical chains. Photochemical generation of free radicals appears to be one of the most probable sources, although it is suggested that metal ions may catalyse autoxidation reactions. Photochemical reactions may be a source of singlet molecular oxygen ($^1O_2$). This is formed by energy exchange between triplet carbonyl and ground state oxygen ($^3O_2$). Singlet oxygen is an extremely active oxidant and it may be produced from oxygen by irradiation in the presence of a wide range of triplet sensitizers. It can also be generated by chemical species. Sensitized photoxidation of amines, sulfides and a variety of organic compounds has been intensively studied.

The role of transition metals as oxidants in aqueous systems requires further investigation. In the presence of complex organic molecules, metal ions may take part in oxidation processes that are closely analogous to biological oxidations mediated by enzymes.

A number of chemical systems mimic the reactions of microsomal oxidases responsible for *in vivo* oxidation of aromatic compounds and other organic compounds foreign to the organism. These oxidases include drug hydroxylase, demethylase, *N*-oxidase, etc. and they require TPNH and molecular oxygen together with a metal. The study of chemical model systems has provided some clues as to the nature of activated oxygen species in enzymic reactions. Fenton's reagent (iron salts, hydrogen peroxide and sulfuric acid) is a source of hydroxyl radicals that will hydroxylate aromatic systems or dealkylate amines or ethers. The active species generated is probably the hydroxyl radical. Typical of such model oxidation systems is that containing ferrous sulfate, ascorbic acid and ethylenediaminetetraacetic acid in a buffer. From a study of the hydroxylation of aromatic compounds in the presence of ferric iron together with hydrogen peroxide and catechol it was proposed that the reactive species was not the hydroxyl radical. Hydroperoxy or peroxy radicals seemed unlikely species because they did not react very well with aromatic systems. The formation of an iron-catechol complex was postulated; this complex was then responsible for direct transfer of oxygen to the substrate. This model system bears some analogy to the iron-porphyrin enzymes. Views of the biological mechanism of oxygen activation involve analogous mechanisms in which cytochrome P-450 forms ferric hydroperoxide-type complexes or ferric superoxide-type complexes with a substrate. The proximity of active oxygen to the substrate permits a concerted reaction.

It would be of interest to determine whether humic acids containing metal ions could function as oxygen transfer reagents. The semiquinones of humic acid alone might function as oxidants, but there is little documentation of the role of nonbiological oxidation in soil. The function of metals may be important. Ferrous iron is known to be oxidized to ferric iron and the latter may act as an oxidant in chemical reactions.

There are few examples of nonbiological oxidation of pesticides. The oxidation of amitrole has been discussed. Aldrin is slowly converted to dieldrin in soils and this reaction is considered to be nonbiological. However, documented instances of environmental nonbiological oxidation not mediated by photochemical action are rare. Examples of catalyzed autoxidations occurring in the absence of light are well documented, but the substrates are usually quite different from pesticides in structure. As was pointed out earlier, pesticides are generally quite stable for long periods in storage, whereas labile molecules subject to fairly rapid oxidation are unlikely to become pollutants.

Reductive Transformations

The 'reduction' of organic compounds usually implies such reactions as the saturation or addition of hydrogen to carbon-carbon, carbon-oxygen, or nitrogen-oxygen multiple bonds. The replacement of halogen by hydrogen is a further example that is important in the case of many pesticide pollutants. In the laboratory, these reactions require vigorous chemical reducing agents or hydrogenation using a metal catalyst. Such conditions are not characteristic of the environment, where reducing reactions must occur under mild conditions. Examples are disproportionation reactions having a low activation energy threshold, or reactions brought about by complex electron-transfer systems. Models for the latter may be constructed if we can postulate the type and role of biological catalysts involved.

Metabolism of toxaphene by rat liver microsomes requires NADPH and anaerobic conditions. Reduced cytochrome P-450 may act as the reducing agent under these conditions. The observation that reduced hematin reacts with toxaphene to cleave C-Cl bonds suggest that iron (II) protoporphyrin systems may provide valuable models for understanding the degradation of some chlorinated hydrocarbons. Mirex also reacted with reduced hematin to give reductive dechlorination products.

Under strongly anaerobic conditions in a flooded soil, toxaphene undergoes extensive alteration and the products appear to be formed by the process of reductive dechlorination.

As stated earlier, the redox potential falls to extremely low values in an anaerobic system and oxidation-reduction potentials as low as -650 mV have been measured. Under these conditions, sulfate is reduced to sulfide and metal salts are reduced. Thus, manganic and ferric salts give manganous and ferrous salts. Subsequent chemical reactions between the metals and hydrogen sulfide give metal sulfides that are stable until they are exposed to oxidizing conditions. Sulfide is then oxidized to sulfate and metal is deposited as oxide or hydroxide.

Reduction of dinitroaniline herbicides proceeds stepwise as the electrode potential is decreased. The sequence proceeds through initial reduction of one nitro group to a phenylhydroxylamine. The second nitro group is then reduced and, after further reduction stages, a m-phenylenediamine is the final product. Reduction potentials for a number of dinitroaniline herbicides were found to be dependent on pH by polarographic techniques. Half-wave potentials for the first polarographic wave for trifluralin were -190 mV at pH 1.5, -540 mV at pH 7.4, and -640 mV at pH 9.2. A second polarographic wave was also distinguishable at higher pH's. Dinitramine was more difficult to reduce than other dinitroaniline herbicides. From these observations it was concluded that a nonbiological pathway for degradation of dinitroaniline herbicides is feasible under anaerobic flooded soil conditions.

Clearly these results imply that a study of redox potentials can be extremely valuable in predicting the type and extent of transformations of pollutants that may occur in sediments under anaerobic conditions.

TRANSMISSION OF SUNLIGHT IN NATURAL WATER BODIES

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The transmission of sunlight into ocean or lake water is a function of the properties of the impinging radiant energy as well as of the water. The significant properties of any source of light, including daylight, are its magnitude, its wavelength distribution, its polarization, and its directional distribution. The significant properties of the water are its absorption and its directional scattering. It is important to recognize that these properties of the light source are entirely independent of each other and that they will be independently altered by the scattering and absorbing properties of the water body.

Most people have a clear concept of the magnitude, wavelength distribution and polarization of light but the directional distribution does not seem to have been generally accepted as one of its significant properties. In fact, directional distribution is the fundamental measurement of the science of radiometry and it cannot be ignored when dealing with the transmission of daylight into natural waters.

When the exact measurement of radiant energy is the primary objective of a study, the study is referred to as the science of radiometry and here we find the critically defined concepts which deal with the geometrical collection of radiant energy and which have been chosen to fulfill theoretical objectives.

When the primary objective of a study is to apply the science of radiometry to lake and ocean water, the effort is referred to as Hydrologic Optics, or Optical Oceanography, and here again we find the geometrical concepts of radiant energy collection, as well as new concepts which apply to the interaction of radiant energy with scattering-absorbing media.

When the primary objective of a study is to determine the biological response of an animal or plant as a function of the radiant energy which is collected or sensed by the animal or plant, it becomes necessary to deal with new problems. In this case we are faced with a dilemma. On the one hand the detectors used by animals or plants do not necessarily collect radiant energy in accordance with the formal geometrical concepts defined in the science of radiometry and hence these formal methods of collection will not necessarily measure the radiant energy actually sensed by the animal or plant. On the other hand, if we simulate the organic sensor by means of a photoelectric detector that duplicates the collecting properties of some specific animal or plant, we may not be collecting energy in accordance with the established geometry of radiometry, and such measurements may not be suitable for use in existing theory.

The basic concept of radiometry is the concept of radiance, illustrated in Figure 1, which depicts a measuring device consisting of a photo-detector at the lower end of a long opaque tube. The purpose of the tube is to restrict the field of view of the photodetector to a fixed solid angle. Radiant energy enters the aperture of the tube along straight lines in the manner illustrated. It can be seen from the figure that if the area of the detector were to be made smaller than illustrated, some of the energy entering the tube would not be detected. The reading obtained with this apparatus is therefore dependent on both the angle of acceptance of the tube and the area of the collector, and the device therefore measures radiant power for a specific solid angle and a specific area. The measurement can be normalized to obtain the radiant power per unit area per unit solid angle and this measurement has been given the name "radiance".

An ordinary camera is a radiance recording device and the image brightnesses formed in its focal plane are proportional to the radiances in the scene.

Measurements of radiance provide an ideal way of examining the details of the underwater light field. For example, Fig. 2 is a photograph taken from a depth of about 10 meters with the camera pointed at the zenith. A 180° wide-angle lens was used and the entire upper hemisphere is consequently compressed onto the film. The horizon is marked by four bright spots around the outside circumference of the exposed area. The picture shows a dark annular ring of nearly uniform density having a width equal to about 1/3 the radius of the exposed area. Inside the annular ring there is a much lighter circular area which exhibits wave details as well as the bottom of the ship. This bright circle is the Snell circle, so called because it identifies the position of the angle of total internal reflection predicted by Snell's law.

Fig. 3 gives radiance data obtained with a radiance tube (see Fig. 1), which shows details of the Snell circle effect. These data were obtained on an overcast day with calm water surface. Curve A was obtained above the water surface and shows changes in radiance of the terrain and reflection by the water surface. Curve B, obtained at a depth of 2.5 cm, shows an increase in radiance near the zenith direction due to optical compression. At the edge of the Snell circle (48.6°) the radiance drops sharply because the path of sight at this angle is reflected downward into the water at an angle of 48.6°. At greater angles the radiance increases moderately until the horizontal direction is reached and then trails off to lower values. Curves C and D demonstrate the loss of these details due to multiple scattering by the water body as the depth of observation increases.

Fig. 4 gives radiance data as a function of depth obtained on a sunny day for three directions, the sun's direction, the zenith direction, and the nadir direction. Near the surface the sun's direction exhibits much higher radiance than the zenith direction but, again due to scattering, these two directions exhibit the same radiance at 40 meters. At still greater depths maximum radiance is found in the zenith direction. It is also of interest that in the first five meters below the water surface the radiance in the zenith direction increases as a result of scattering by particles in the water.

Fig. 5 is a recording of the radiance distribution in the plane of the sun obtained on an overcast day at a depth of about 43 meters. The values of radiance in the lower hemisphere have been multiplied by 10 in order to show the distribution more clearly. It can be seen that light from the upper hemisphere arrives mainly from the zenith direction whereas light from the lower hemisphere arrives mainly from the horizontal direction.

Fig. 6 compares the magnitude and shape of the radiance distribution in the plane of the sun at two depths. In "A" the maximum radiance value is in the direction of the sun and the distribution is distorted in that direction. In "B" the maximum radiance value is much closer to the zenith direction and the distribution is more nearly symmetrical around the zenith direction. These changes in magnitude and shape of the radiance distribution are due to the water properties only.

In addition to providing a detailed description of the light field, radiance distribution data of this kind can be used to calculate other radiometric quantities which are useful for quantitatively describing the transmission of daylight into natural waters. Figure 7 indicates the mathematical procedure for calculating scalar irradiance h and the vector irradiances H(+) and H(-) from radiance distribution data. The figure also shows the procedure for calculating the irradiance reflectance R and the absorption coefficient a from these irradiances.

Scalar irradiance describes the total radiant energy arriving at a true point. Since it is not possible to make an instrument that will measure at a true point, a substitute measurement of spherical irradiance has been defined, which is directly proportional to scalar irradiance. The concept of spherical irradiance is illustrated in Fig. 8. Its measurement requires a diffuse spherical collector having uniform collecting properties for all directions. Figure 8 illustrates several parallel bundles of radiant energy impinging on such a sphere from different directions. In a real measurement, bundles such as those shown would be arriving from all directions and the sphere would respond equally to each bundle. Practical collectors of this kind have been built and are in use in research studies dealing with the effect of pollutants on the growth of phytoplankton.

The concept of vector irradiance is illustrated in Fig. 9. This measurement requires a flat collector that collects radiant energy in accordance with the cosine of its angle of incidence on the collector. In Fig. 9 four bundles of radiant energy are shown impinging on such a collector at different angles. Each bundle is accompanied by an equation which indicates the fraction of the bundle that is collected. Practical collectors for determining vector irradiance have been developed and are available commercially.

Measurements of vector irradiance have been used to record the spectral distribution of radiant energy underwater, the spectral reflectance of the radiant energy, and the spectral attenuation of the radiant energy as a function of depth in natural waters.

Figure 10 gives monochromatic measurements of the downwelling irradiance (H-) as a function of depth in ocean water containing a low concentration of phytoplankton. Fig. 11 gives similar data for lake water containing a high concentration of phytoplankton and also decomposition products. Note that the ordinate and abscissa scales are the same in both figures and that in Fig. 10 the depths for measuring downwelling irradiance are at 5m 15m and 25m whereas in Fig. 11 the depths of measurement are for each meter down to a maximum of 10m. The absorption of long wavelengths exhibited in Fig. 10 is largely due to absorption by water. This absorption is also seen in Fig. 11 and in addition Fig. 11 exhibits strong absorption in the blue region of the spectrum due to phytoplankton pigments and soluble decomposition products. Figures 12 and 13 give reflectance data for similar bodies of water.

Figure 14 illustrates the attenuation of irradiance with depth for 5 wavelengths. Except for some local effects that occur near the air-water interface, these data can be described and predicted by an exponential law of attenuation shown in equation 1.

$$\frac{H_2}{H_1} = e^{-K\Delta Z} \qquad (1)$$

The experimental fact that the exponential law can be applied to the transmission of daylight into natural waters is of great importance for the ecologist because it provides a way for separating the total attenuation coefficient of ocean or lake water into parts which apply to the separate components found in these waters and this, in turn, makes it possible to determine the quantum efficiency of in situ photosynthesis and the effect of environment on productivity.

The exponential law of attenuation can be written with depth as the only parameter as is done in equation 1 or it can be written to include both depth and concentration as in equation 2.

$$\frac{H_2}{H_1} = e^{-KC\Delta Z} \qquad (2)$$

In current research at S.I.O. I have used the exponential law in the form shown in equation 3 where K_w and the coefficients on the right of the equal sign are the attenuation coefficients of the components of ocean water which are of interest. H_1 and H_2 in equation 3 are measurements of irradiance at the upper (H_1) and lower (H_2) surfaces of a selected depth interval ΔZ. K_w is the attenuation coefficient of clean water alone. Since K_w can be evaluated from measurements in clean ocean water, all factors at the left of the equal sign in equation 3 are known.

$$\frac{\ln\frac{H_1}{H_2}}{\Delta Z} - K_w = K_1C_1 + K_2C_2 + K_xC_x \qquad (3)$$

At the right of the equal sign, K_1C_1 represents the attenuation coefficient per meter of living phytoplankton pigments at a concentration of C_1; K_2C_2 similarly represents the attenuation coefficient of the pheopigments (that is, the non-living phytoplankton pigments); and K_xC_x similarly represents the attenuation coefficient of the unidentified absorbing materials.

To use this form of the exponential law it is necessary to locate ocean water for which K_xC_x is not significant. Figure 15 shows the results of a study made during the S.C.O.R. Discoverer Expedition of 1970 in which the optical density of 10-meter-thick layers of ocean water were measured in situ. In Fig. 15 these densities are plotted against the combined concentrations of living (C_1) and non-living (C_2) plant pigments. In this plot, if the measured density is due only to living and non-living plant pigments at various concentrations, the data will plot along a straight line originating on the ordinate at the density of clean ocean water. If on the other hand the measured density of a 10 meter layer is due in part to a component other than plant pigments the data point will plot higher than the aforementioned line by an amount equal to the excess density over that due only to the plant pigments C_1 and C_2. The straight line in Fig. 15 starts on the ordinate at the optical density determined for clean ocean water and passes through the data points of minimum density obtained at a number of ocean stations. The equation for this line is given by equation 4,

$$\frac{\log \frac{H_1}{H_2}}{\Delta Z} - K_w = (C_1 + C_2)k \qquad (4)$$

where k (the slope of the line) would represent the average attenuation coefficient per meter per unit concentration for the combined living and non-living plant pigments. The analytical determinations of chlorophyll-a and pheopigments for these low density samples showed significant differences in the ratio of these two classes of pigments and made it possible by means of simultaneous equations to evaluate K_1 and K_2 using equation 5,

$$\frac{\log \frac{H_1}{H_2}}{\Delta Z} - K_w = K_1C_1 + K_2C_2 \qquad (5)$$

on the basis that K_xC_x was insignificant for the low density samples. It was then possible to determine, by difference, the value of K_xC_x in samples which showed high values of optical density due to components other than plant pigments. A second application of the exponential law to the independent computed values of K_1C_1, K_2C_2, and K_xC_x was then used to compute the absorption, per 10 meters of sample thickness, of the independent absorbing components and these values can be normalized to make their sum equal to the total absorption already obtained from measurements.

From these latter calculations the radiant energy absorbed by the viable plant pigments is obtained and this is expressed in quanta absorbed per unit volume per 6 hours of time (noon to sunset). From additional analytical work performed on samples of the same ocean water we have measurements of the carbon-14 fixed by the phytoplankton per unit volume per 6 hours of time (noon to sunset), and from the ratio of these two pieces of data we can calculate the quantum efficiency of photosynthesis by the in situ mixed phytoplankton population.

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The In Situ Quantum Efficiency of Natural Phytoplankton Populations, John E. Tyler. Limnology and Oceanography, vol. 20, #6, pp.976-980. Nov. 1975.

THE CONCEPT OF RADIANCE

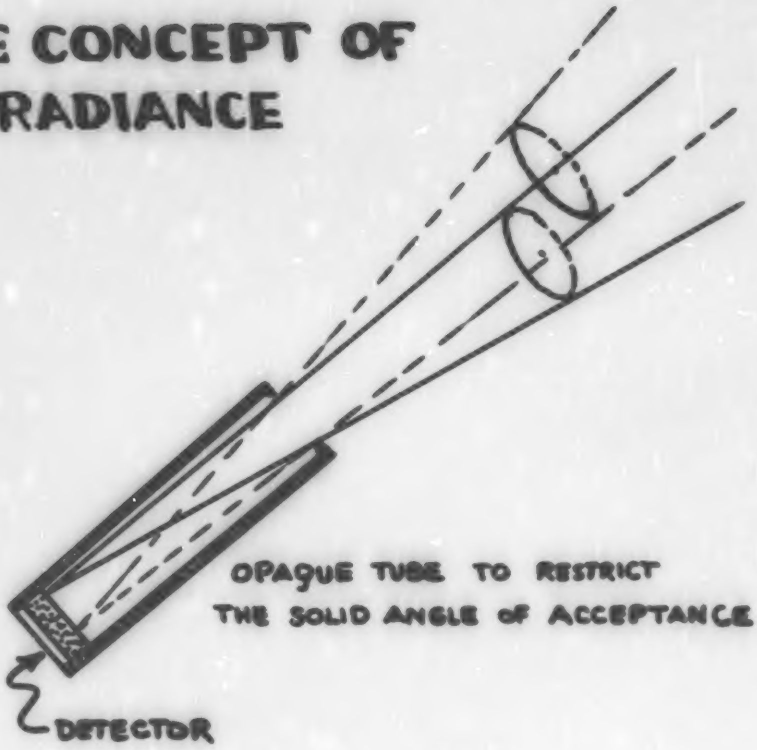
OPAQUE TUBE TO RESTRICT
THE SOLID ANGLE OF ACCEPTANCE
DETECTOR

Fig. 1 The figure illustrates the collection of radiant flux from a diffuse source such as the sky. The total radiant flux that can reach the detector depends on the area of the detector and the solid angle of acceptance of the opaque tube.

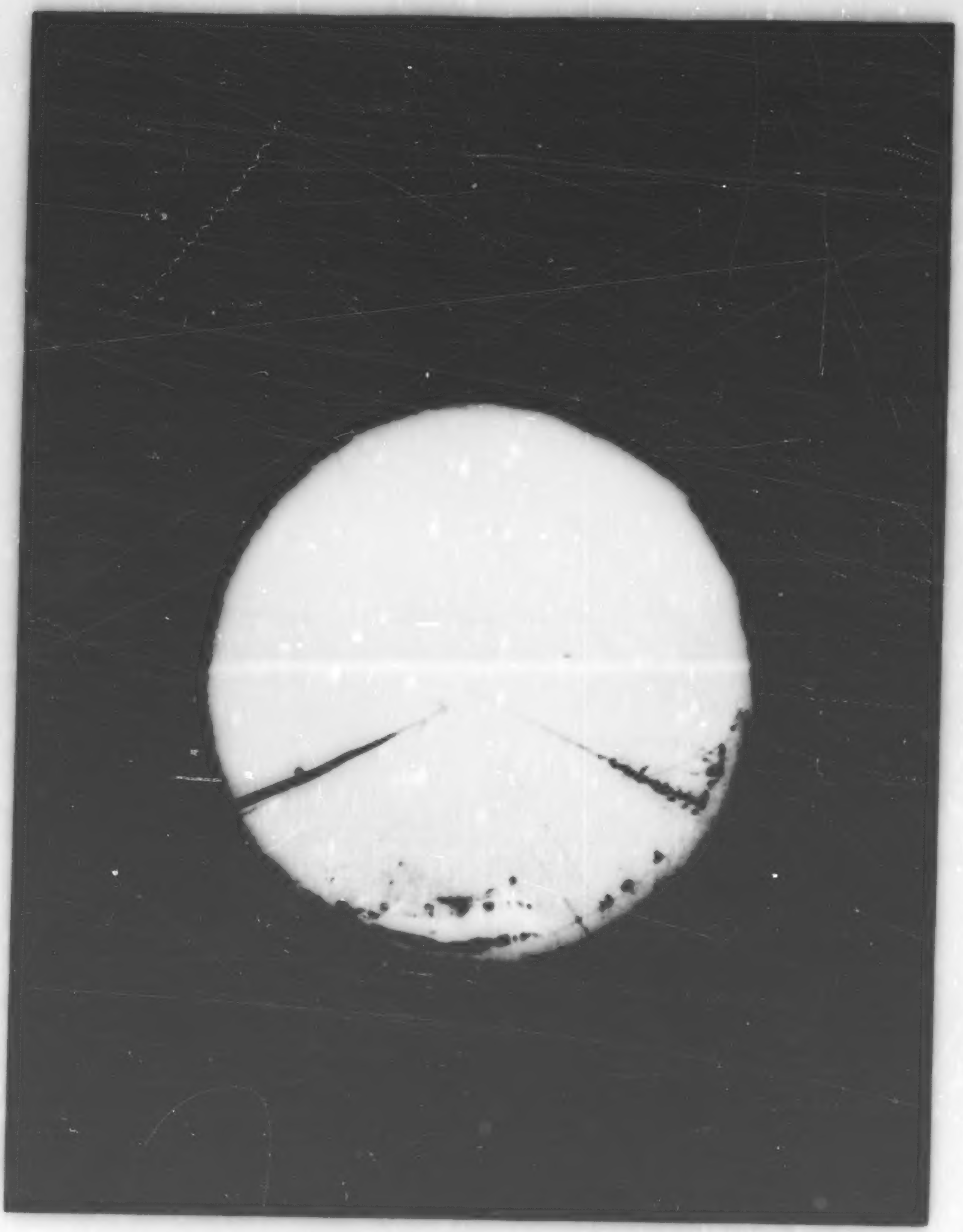

Fig. 2   Photograph in the zenith direction from 10 meters showing the Snell circle, with details of the ship. The four bright spots separated by 90° mark the horizontal direction underwater,

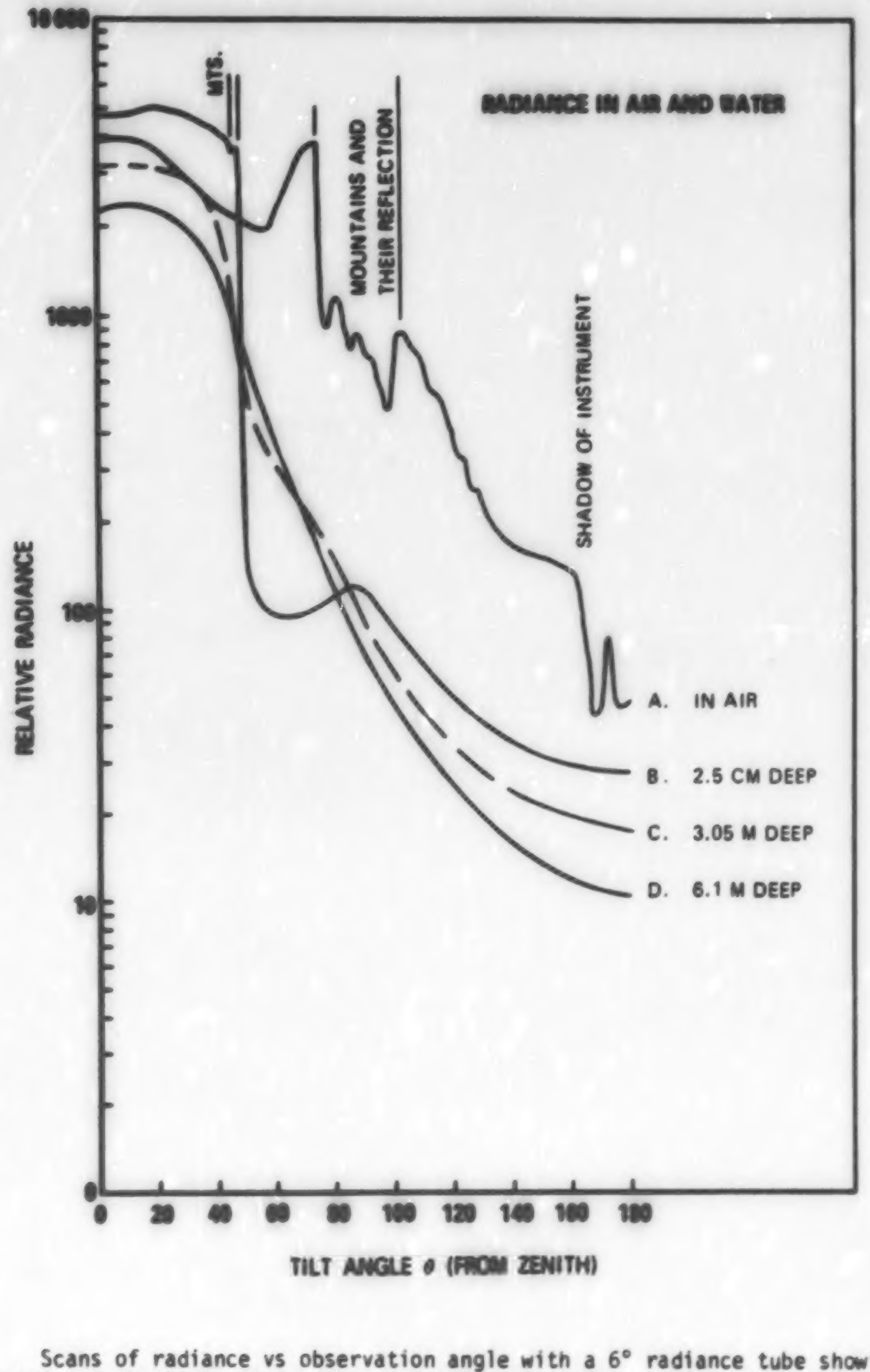

Fig. 3 Scans of radiance vs observation angle with a 6° radiance tube showing the details of the light field above and below the water surface, the latter at different depths. Overcast day.

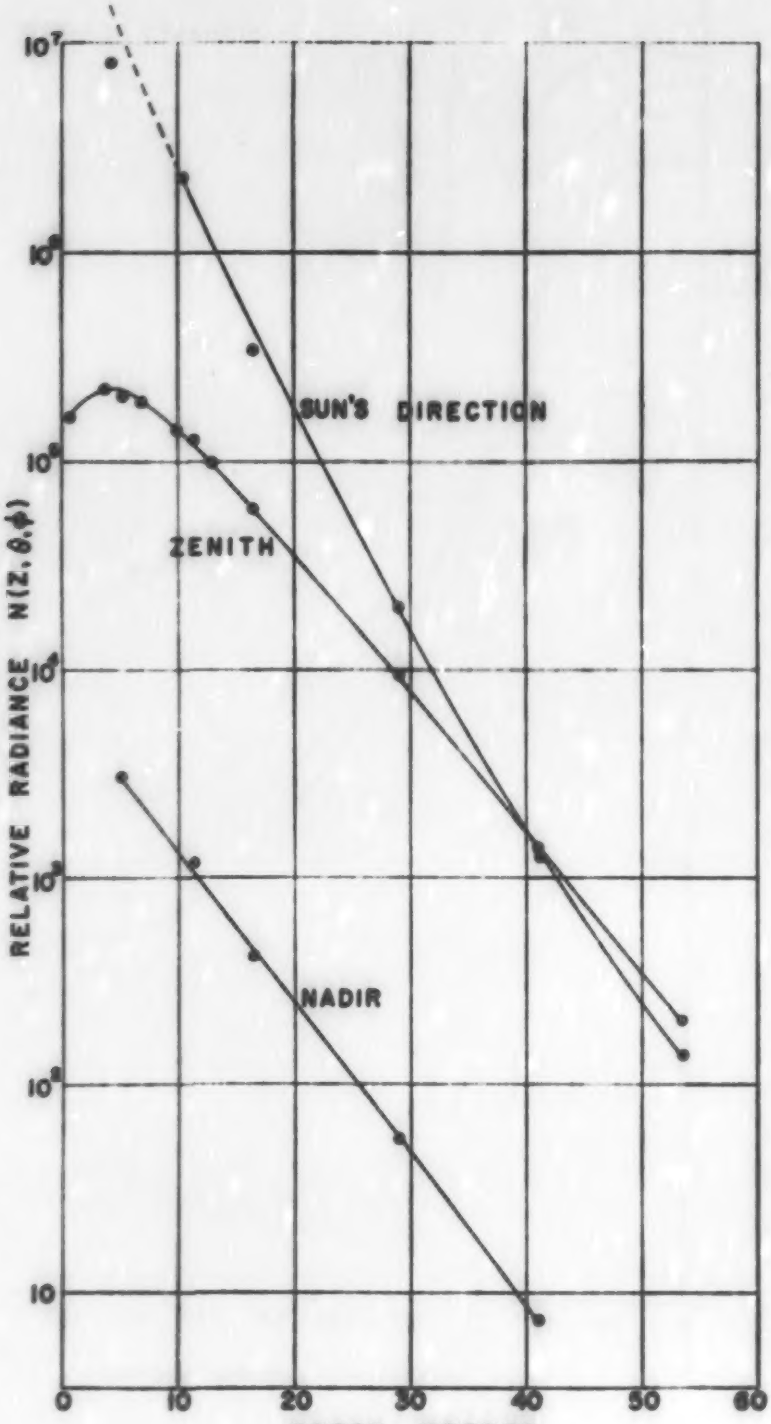

Fig. 4 Scans of radiance vs depth for fixed angles of observation. Sunny da

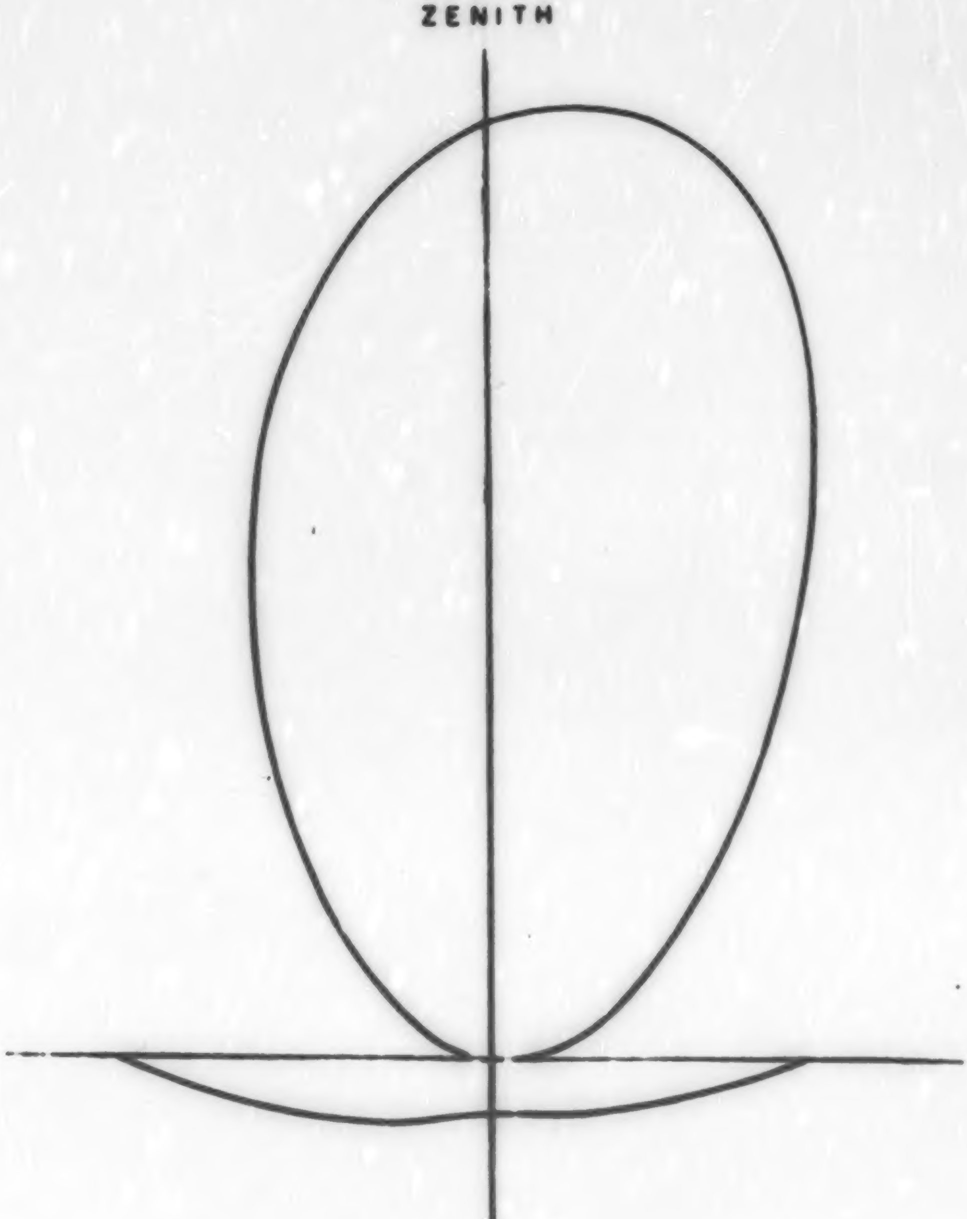

Fig. 5 Relative shapes of the radiance distribution in the upper and lower hemispheres at a depth of 43 meters. Lower hemisphere data has been multiplied by a factor of 10.

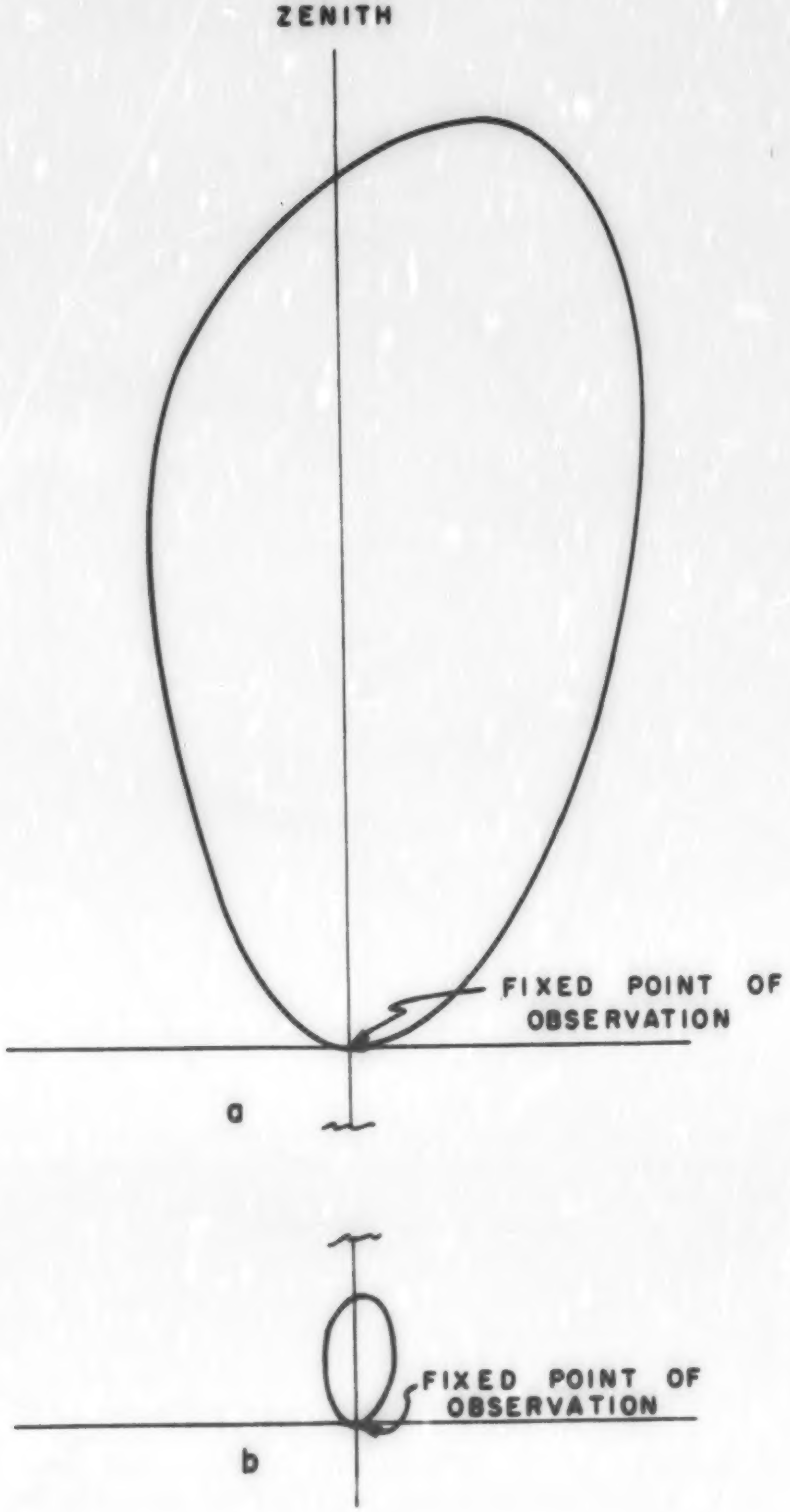
ZENITH
FIXED POINT OF OBSERVATION
a
FIXED POINT OF OBSERVATION
b

Fig. 6 Radiance distributions at two depths showing changes in shape and i magnitude.

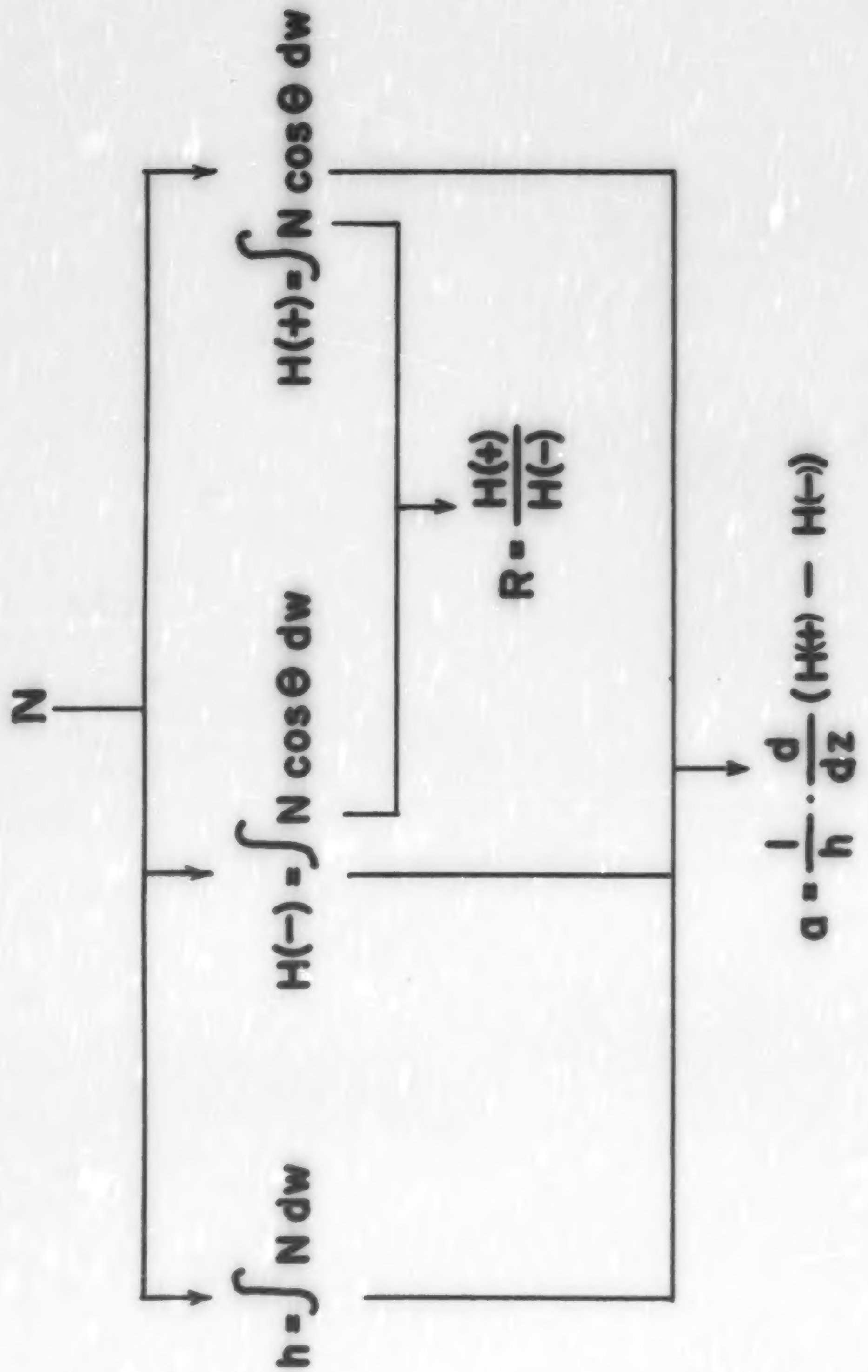
N
H(+) = ∫N cos Θ dw
H(−) = ∫N cos Θ dw
h = ∫N dw
R = H(+)/H(−)
a = 1/h · d/dz (H(+) − H(−))

Fig. 7 Computational procedures for computing the irradiances, reflectance and absorption coefficient from radiance data.

THE CONCEPT OF SPHERICAL IRRADIANCE

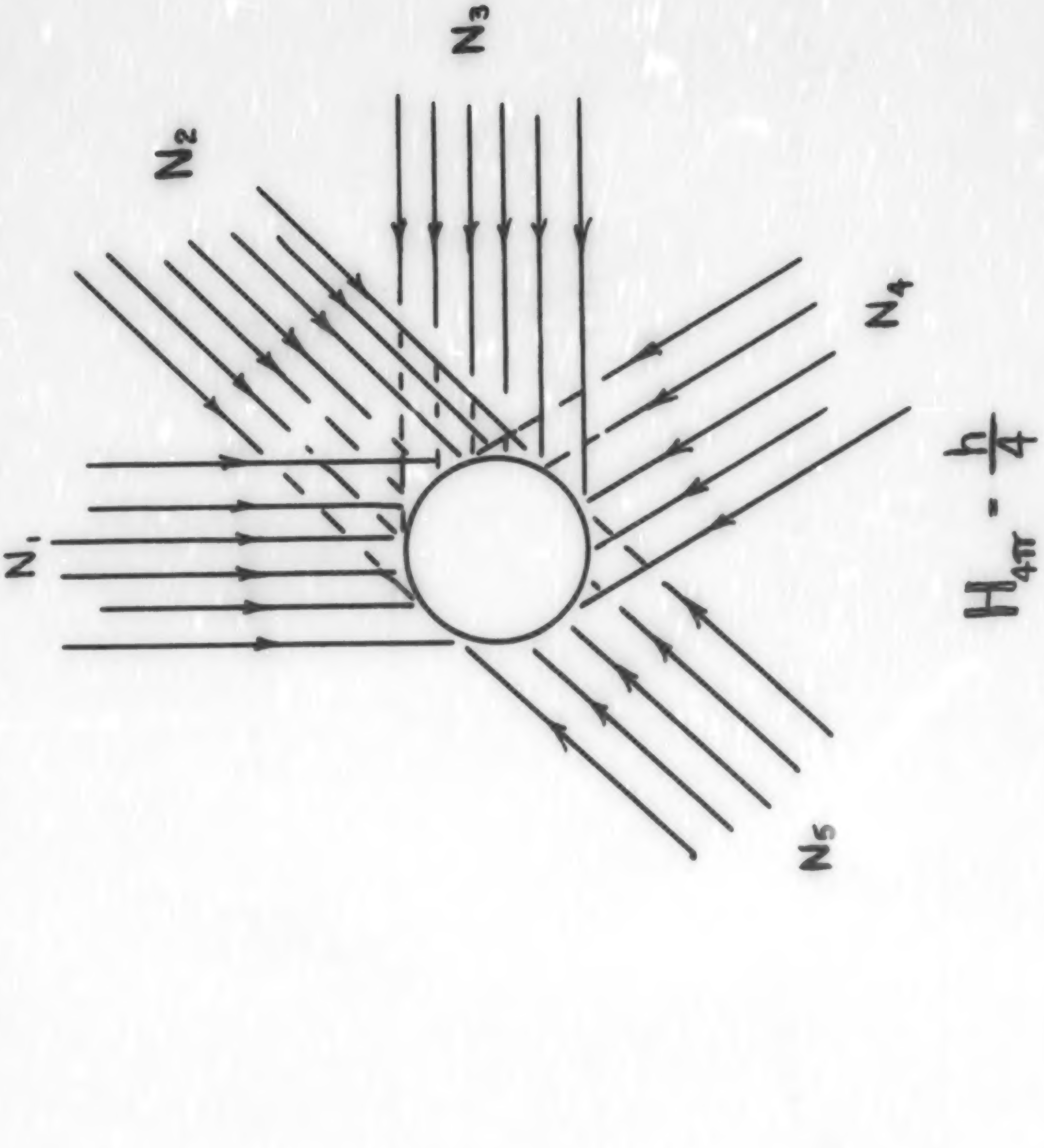
N_1
N_2
N_3
N_4
N_5
$H_{4\pi} - \frac{h}{4}$

Fig. 8 The figure illustrates the concept of spherical irradiance. The diffusing sphere is designed to collect equally from all directions.

THE CONCEPT OF IRRADIANCE

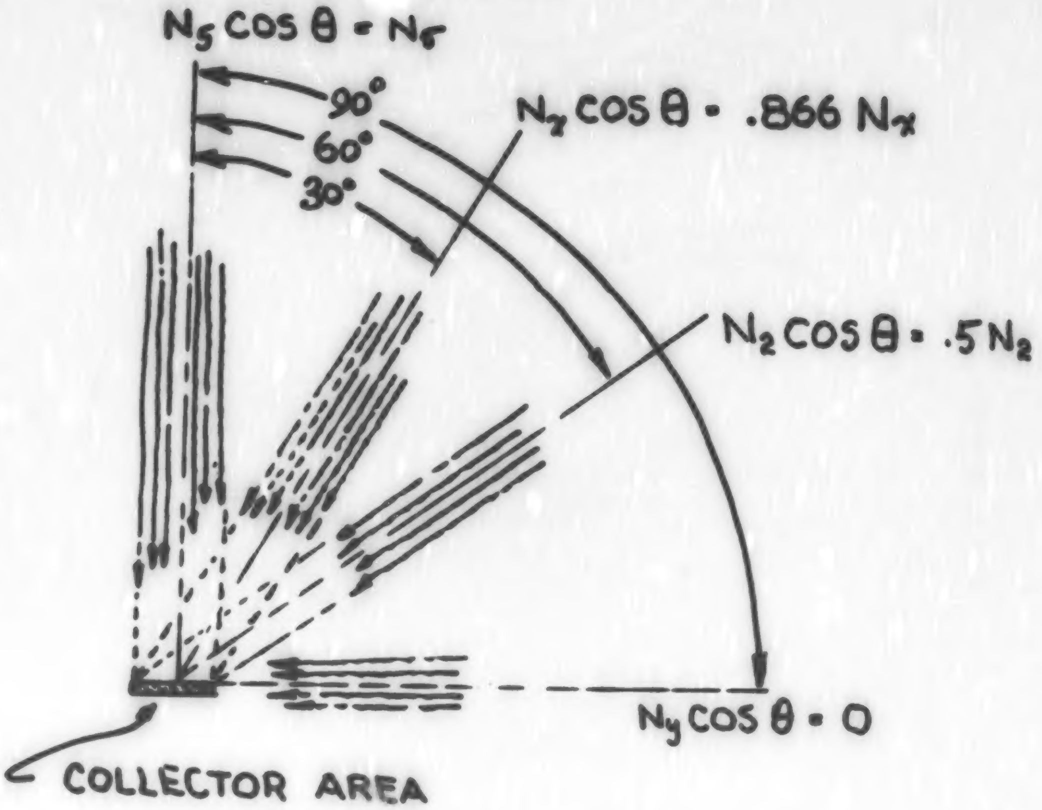
N5 COS θ = N5
90°
60°
30°
Nx COS θ = .866 Nx
N2 COS θ = .5 N2
Ny COS θ = 0
COLLECTOR AREA

Fig. 9 The figure illustrates the cosine collecting properties of a horizontal collector of fixed mechanical area whose apparent area depends upon the angle of incidence of the bundle of incoming rays.

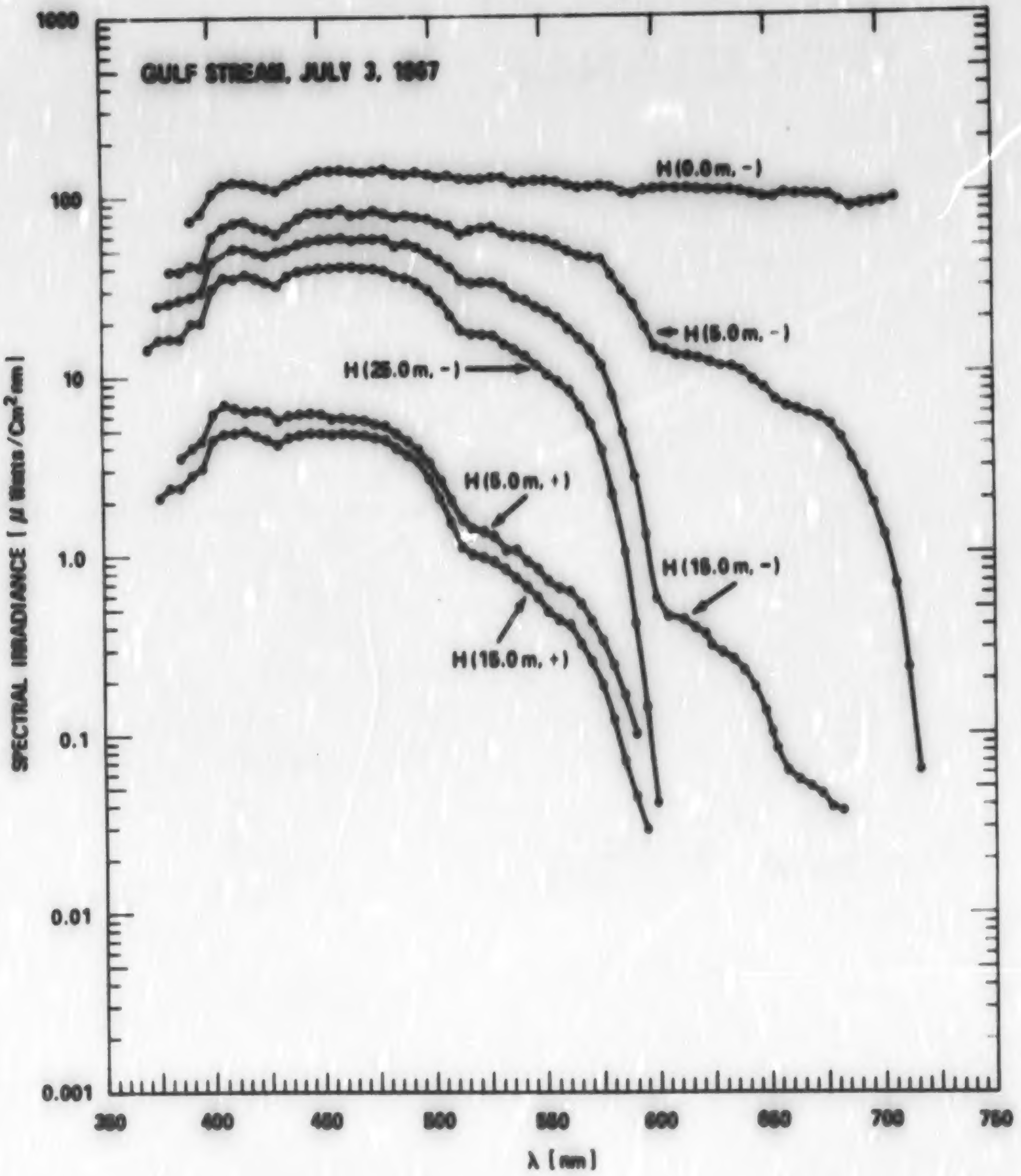

Fig. 10 Irradiance measurements as a function of wavelength in the Gulf Stream.

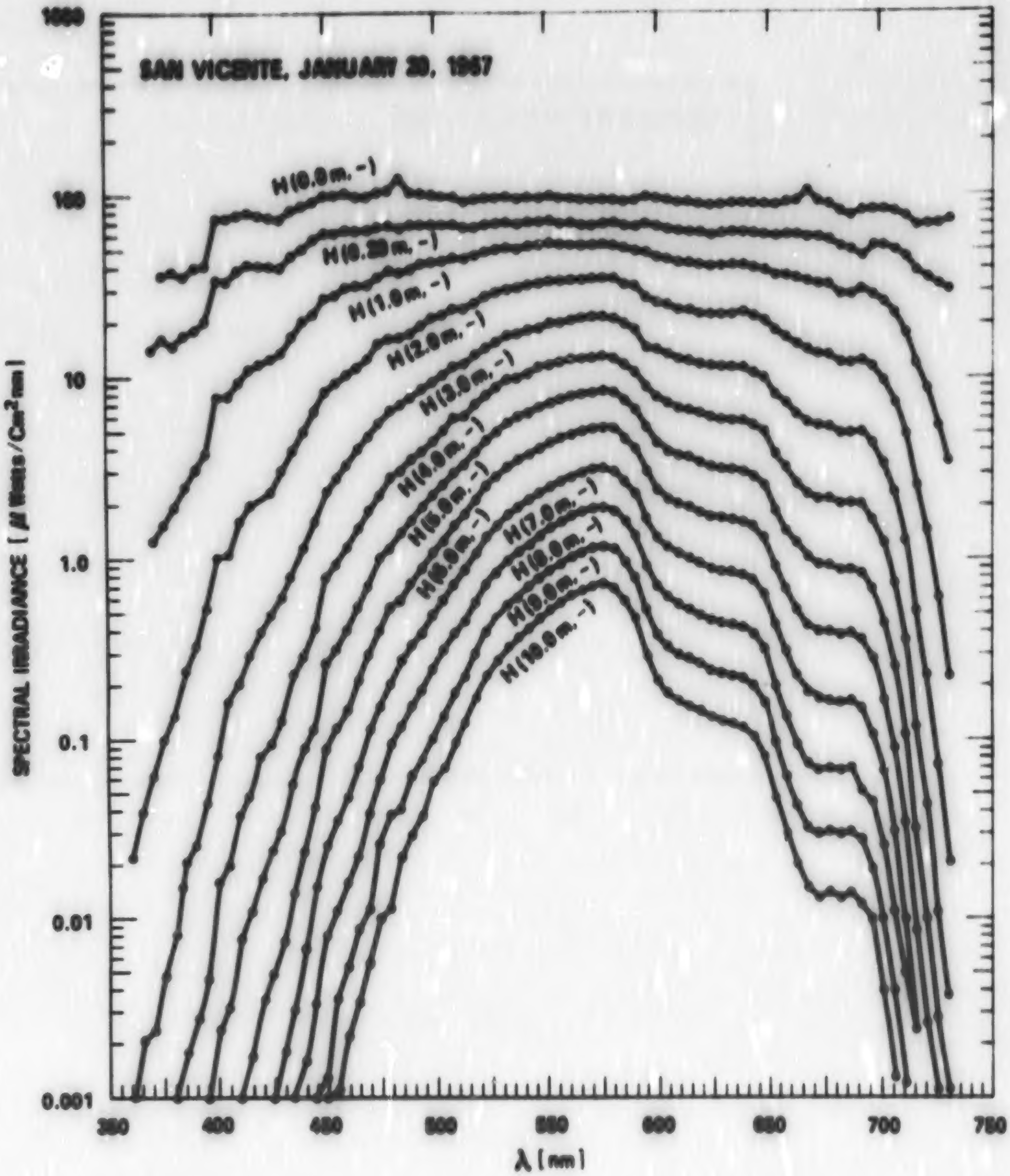

Fig. 11 Irradiance measurements as a function of wavelength in a eutrophic lake.

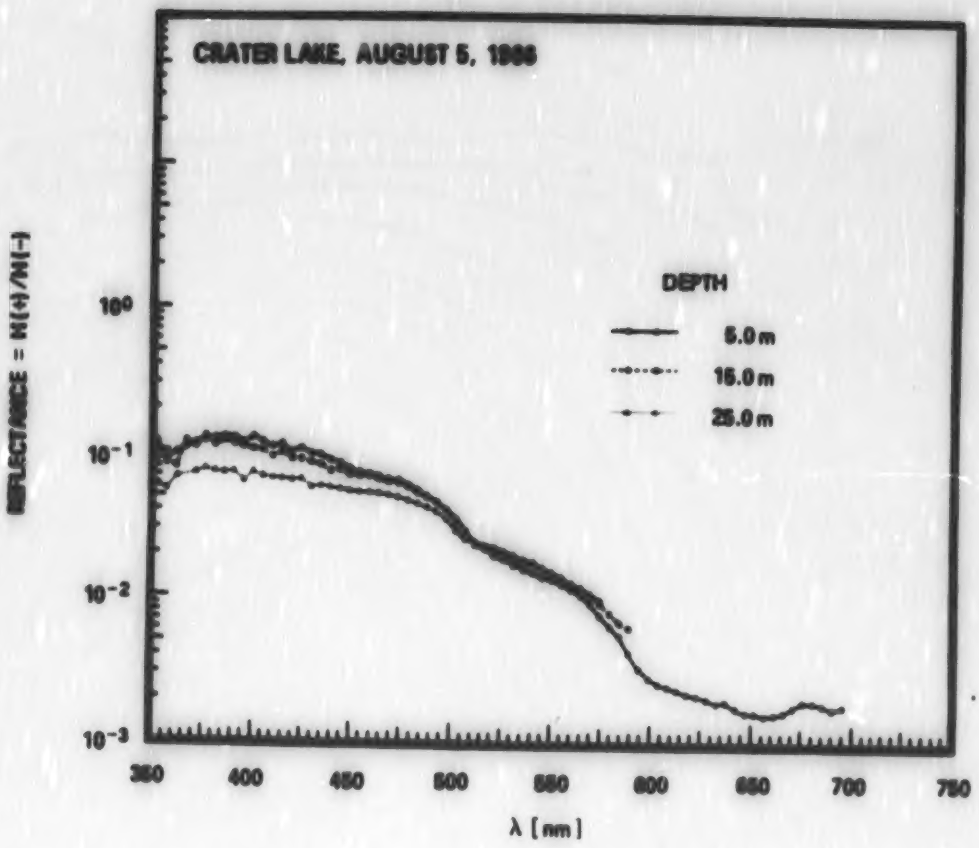

Fig. 12 Reflectance data obtained in Crater Lake, Oregon.

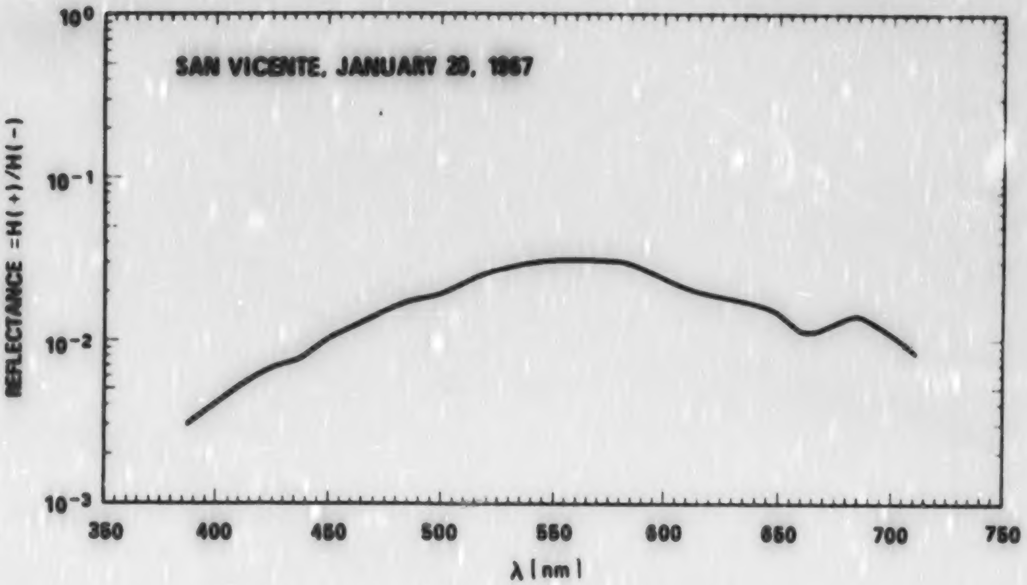

Fig. 13 Reflectance data obtained in a eutrophic lake.

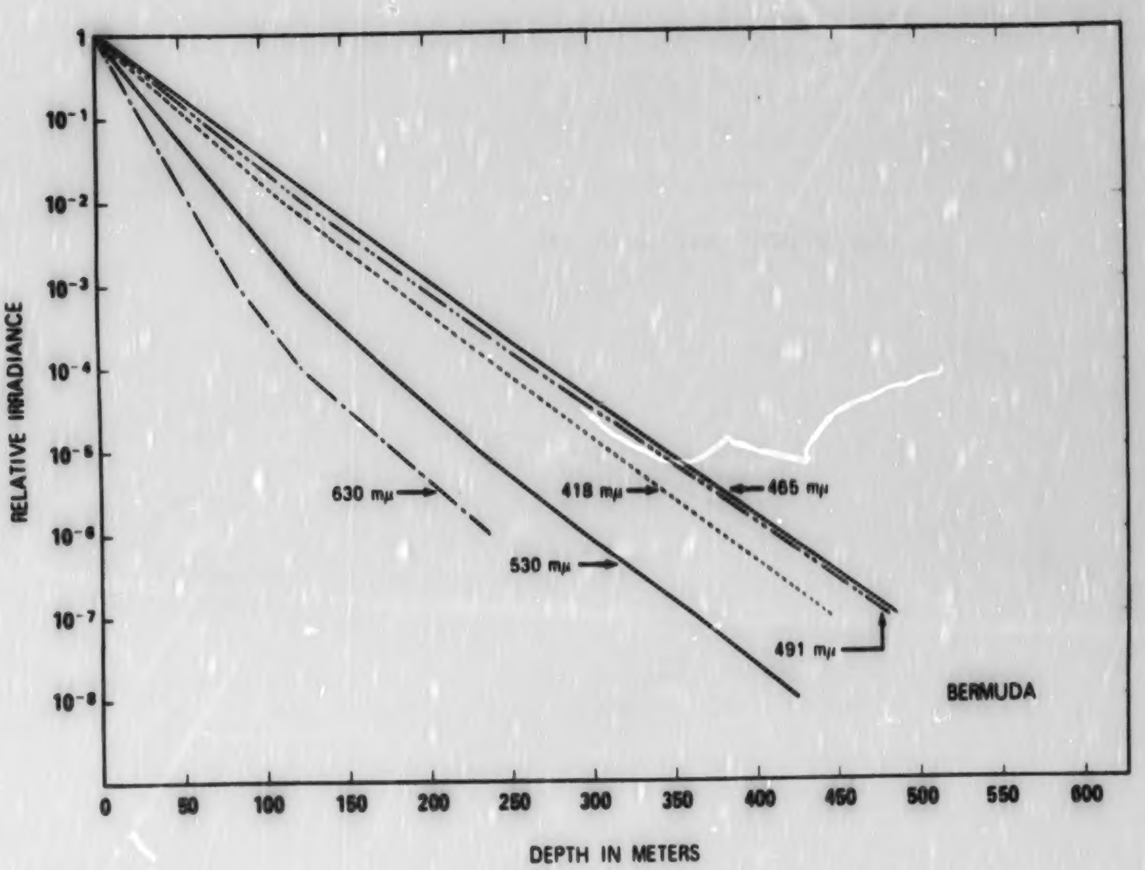

Fig. 14 Attenuation of irradiance with depth for 5 wavelengths in clear ocean water.

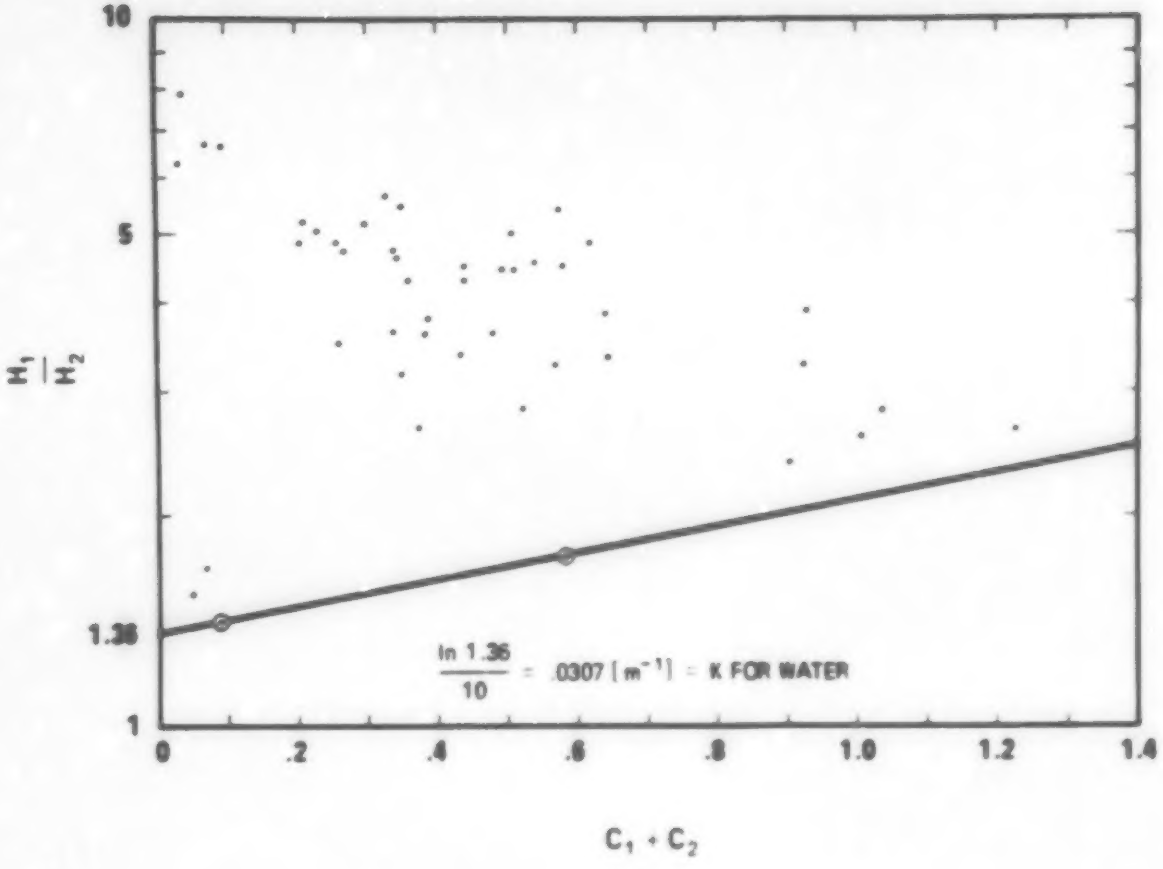

Fig. 15 Plot of optical density of 10-meter layers of ocean water vs the combined concentrations of viable phytoplankton pigments and phaeopigments.

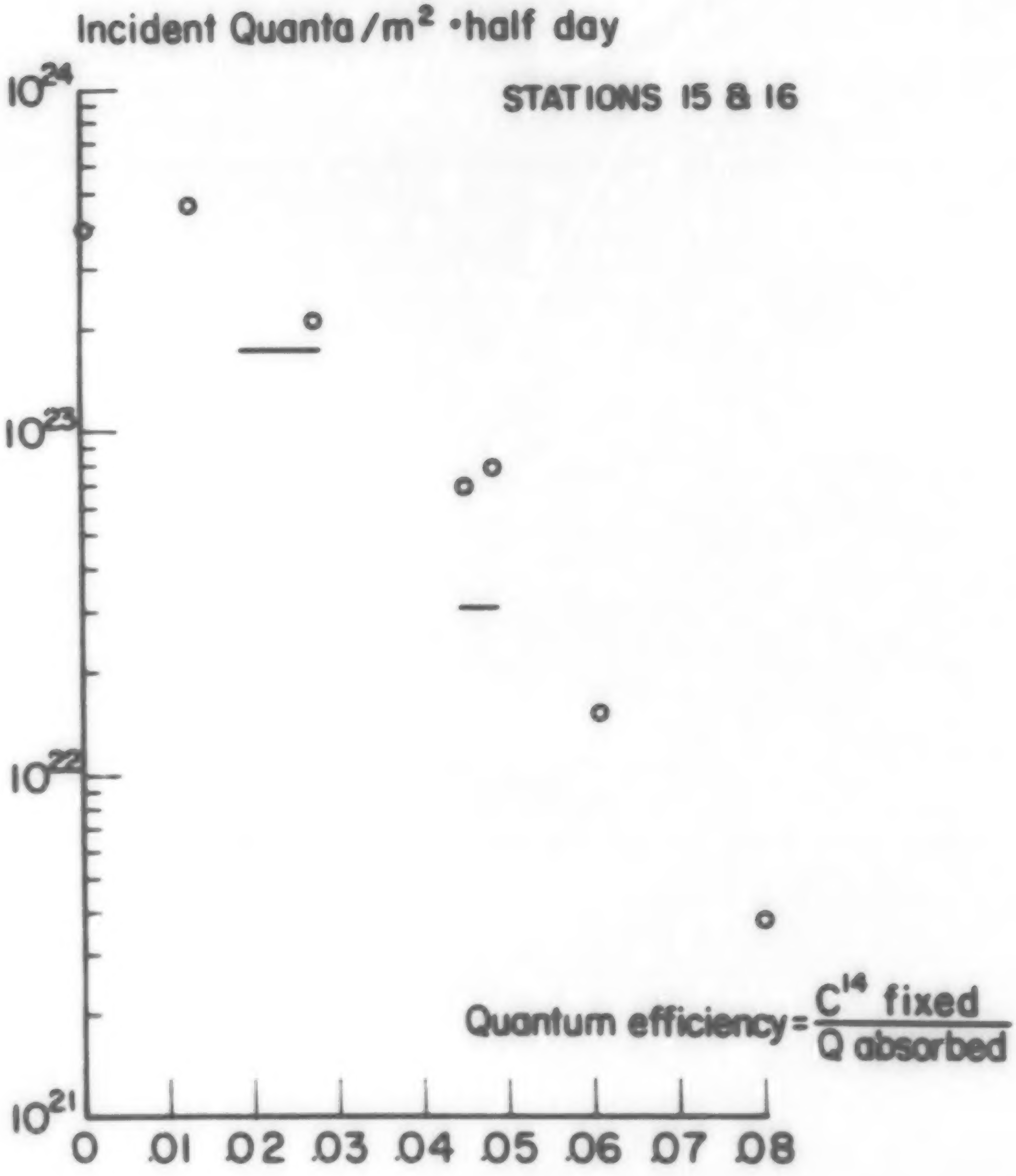

Fig. 16 Plot of the quantum efficiency of photosynthesis in the ocean vs the incident irradiance, the latter determined by the depth of the phytoplankton.

PREDICTION OF ACTIVITIES OF ELECTROLYTES IN NATURAL WATERS

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The earliest and simplest ways of predicting the properties of mixtures of electrolytes were developed by MacInnes (1919), Harned (1920), and Lewis and Randall (1921). They developed the ionic strength principle which says that the activity coefficient of an ion is a function only of the ionic strength and the mean salt method, which says that the activity coefficient of potassium is the same as that of chloride in KCl. These two approximations are still used in most of the calculations of the speciation of natural waters. Later the Debye-Hückel limiting law (1923) gave the theoretical basis for predicting very dilute solutions. A better method of predicting mixtures was developed by Brønsted (1923), and Guggenheim (1935) who combined the Debye-Hückel limiting law with the assumption that positive ions had uniform interactions with each other. In 1953 T. F. Young and M. B. Smith showed that the ionic strength principle could be improved by applying it to the total solution rather than to partial molal properties. Young's rule states that the change in volume on mixing two components at the same ionic strength is zero. This rule can equally well be applied to heats and free energies and it is far superior to the ionic strength principle. Scatchard (1932, 1961) added triplets and higher terms to the basic assumptions of Brønsted and Guggenheim. Wood and Smith (1965) showed that the interactions of two like charged ions were not uniform and had to be taken into account for accurate calculations. From a knowledge of the important interactions, equations were developed for predicting the properties of charge symmetric mixtures (Wood and Anderson (1966), and Guggenheim (1966)). The way in which these equations were developed shows that they are essentially Young's rule applied to an appropriate set of components of the mixture together with corrections for the like-charged pair interactions and some of the triplet interactions. Following this several different methods were developed for extending the calculations to charge asymmetric mixtures. Reilly and Wood (1969), Scatchard, Rush, and Johnson (1970), Reilly, Wood, Robinson (1971) and Pitzer (1973). These equations are capable of giving accurate estimations of the activity coefficients of mixtures of strong electrolytes even at ionic strengths above 1 molal. Thus they should give accurate predictions of seawater and all natural waters except the very concentrated brines. The success of Reilly, Wood and Robinson equations in predicting the activities of the major components of seawater with as much accuracy as they have been measured is demonstrated.

The equations do not work for mixtures in which the components have strong association and this is the area where current developments are needed. It should prove possible to combine the methods developed for mixtures of strong electrolytes with the normal ion-pairing approach to produce a set of more accurate equations. The possibilities and pitfalls in this procedure are discussed. Another important area for future work is in the development of methods of making measurements of the activities of trace components so that the speciation models being developed can be tested.

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